Feasibility of a Dutch Process for Microbial Desulphurization of Coal

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ABSTRACT

The technical and economical feasibility of microbial coal desulphurization has been studied with attention on the removal of finely dispersed inorganic sulphidic minerals which cannot be removed by sink-float processes.

Data have been collected on the suitability of various low-sulphur coals representative of future Dutch imports. It was possible to remove 90% of the pyrite present within 8 to 10 days by using a mesophilic, pyrite-oxidizing, microbial system. No removal of organic sulphur was observed. Depending on the type of coal, a considerable reduction in the contents of ash-forming minerals and heavy metals was achieved.

To determine the optimal dimensions of a reactor system, the kinetics of bacterial growth and pyrite oxidation were studied. The kinetics of bacterial pyrite oxidation appear to be first order in the amount of pyrite present, indicating a plug flow reactor is most appropriate. However, because almost all of the bacterial biomass is attached to the solids, incoming coal in a continuous working system can be inoculated only by intensive contact with particles already loaded with bacteria. For this purpose, a plug flow reactor is not adequate, and a configuration consisting of a mixed flow reactor followed by a plug flow is proposed. To prevent biomass limitation, the residence time in the mixed flow reactor must be longer than the reciprocal value of the specific growth rate of the pyrite oxidizing bacteria, 0.05 h^{-1} at pH 1.8.

The slow kinetics and the enormous amounts of coal to be treated require huge reactors. To make the process economical, the reactors must be simple and cheap. The choice is a cascade of Pachuca tank reactors. The first tank functions as the mixed flow reactor. The following tanks, in series, approximate a plug flow. Studies on oxygen mass transfer, mixing and settling in laboratory scale Pachuca tank reactors revealed that the air flow required for the oxygen supply of the pyrite-oxidizing microflora is enough for adequate suspension and mixing of the coal in the water and to prevent settling.

From the kinetic and technological studies a process design has been derived. This has been adopted by an engineering consultancy firm to calculate the cost of the process. It appears that, depending on the coal types to be cleaned, the location and governmental environmental regulations, microbial desulphurization might be a realistic option.

INTRODUCTION

Coal mining has had a long tradition in The Netherlands, beginning in the Middle Ages, but ending during the 1960's when all Dutch coal mines were closed down for economic reasons. At that time, rich sources of natural gas and cheap imports of oil were available to meet the Dutch requirements. Moreover, a considerable increase in the exploitation of nuclear energy was expected to occur. However, after the first and second energy crises and public concern about the use of nuclear energy, a significant increase in coal imports and utilization have been expected, but the re-opening of the Dutch coal mines still remains unrealistic for economic reasons. To reduce the environmental control requirements when burning coal on a large scale, an extensive government funded Dutch research programme has been started in order to develop clean coal technology. Studies have been started on coal gasification and liquefaction, and on fluidized bed combustion. One of the research programmes was focussed on the technical and economical feasibility of different coal cleaning techniques: high gradient magnetic separation (HGMS), electrostatic separation (ESS) and microbial desulphurization. The aim of this programme was to collect data to enable the Dutch government to compare these three processes, all of which are aimed at the removal of inorganic sulphur compounds.

This paper deals with the Dutch feasibility study on microbial coal desulphurization. Its aim is to present a survey of the strategy that has been followed in order to complete a process design which has allowed the evaluation of its technical feasibility and the completion of a reliable cost analysis. For that reason, this paper will not give all of the details of the extensive research programme.

PRINCIPLE OF MICROBIAL DESULPHURIZATION OF COAL

The biological cleaning technique is based on the ability of some acidophilic bacteria, of which *Thiobacillus ferrooxidans* is the best known, to oxidize sulphur containing minerals, especially pyrite, which is the most important inorganic sulphur compound in coal. The principle has already been known for a long time. Zarubina et al. [1] were the first to mention the possibilities. Since then, an impressive number of publications have appeared. These, in general, supported the idea that acidophilic pyrite oxidizing bacteria can remove inorganic sulphur compounds from coal. Bos et al. [2] have reviewed these studies. Desulphurization of coal can be accomplished in two different ways. In the first, the bacteria oxidize as much of the inorganic sulphur compounds in the coal as possible (the complete oxidation process). This is the most popular. In the second, bacteria are used only initially to change the surface properties of the pyrite particles. This enables the use of physical separation techniques, such as oil agglomeration and flotation to remove pyrite from the coal. Origi-

nally, in the Dutch studies on microbial desulphurization of coal, attention was paid to both possibilities. However, the results obtained by Doddema [3] indicated that the combination with oil agglomeration promised little. As a result, Dutch activities have concentrated on complete oxidation.

Over the years, microbial desulphurization of coal has met with much skepticism. The main disadvantages are the slow rates of pyrite oxidation, the inability of the acidophiles to oxidize organic sulphur compounds present in the coal, and the production of a low pH waste water rich in iron and other metals, which requires further treatment. Data on the technical and economical feasibility are scarce. Estimates on the cost have been published by Detz and Barvinchak [4].

OUTLINE STRATEGY

In order to be able to complete a technical and economical feasibility study, data have been collected on the suitability of the microbial desulphurization process for a variety of different coals, representative of future Dutch coal imports. The results of the leaching have not only been evaluated in terms of pyrite removal, but also the starting materials and the products have been characterized by proximate and ultimate analysis and by different advanced analytical techniques (such as SEM-EDS) [2,5]. Attention has also been paid to the size distribution of minerals and the effect of the degree of association of pyrite particles with the coal matrix on the leaching results [6].

Kinetic data on the growth of the pyrite oxidizing bacteria and the pyrite oxidation, itself, in mixtures of coal and water were necessary.

For a detailed reactor and process design, not only the data from these applied microbiological studies, but also technological data must be collected. From the start of the studies, it was realized that for economic reasons a simple, and therefore comparatively cheap, reactor system is required. It has been concluded that a gas-agitated slurry reactor offers the best prospects for the treatment of the low sulphur coals of interest. One of the simple reactor types which fits these requirements is the Pachuca tank which is cylindrical with a conical bottom. Air is jetted in at the bottom. The air flow will agitate the coal slurry, which results in an upward stream in the middle of the tank and a downward stream in the outer parts. Oxygen transfer from the air to the liquid phase takes place mainly in the upward stream [7].

An optimal leaching process demands that everywhere in the reactor system oxygen depletion and accumulation of solid materials by sedimentation must be prevented. Therefore, data on relevant physical phenomena (oxygen mass transfer, mixing and sedimentation) in mixtures of pulverized coal in water in Pachuca tanks was needed.

Integration of microbiological and physical technological data has resulted in a rather detailed process scheme for a 100,000 metric ton/year (Mg/y) in-

stallation, which was designed in order to make a cost analysis. Finally, it was possible, taking into account the Dutch governmental standards for the maximal sulphur concentration in coals being used for energy generation, to assess the potential of the microbial desulphurization process.

RESULTS OF APPLIED MICROBIOLOGICAL STUDIES

The results of the applied microbiological studies, in which a mesophilic mixed culture originating from a coal washing plant were used, confirm in many respects the results of other investigations into the microbial desulphurization of coal [2,5]. All coal samples, originating from various parts of the world, appeared to be susceptible to microbial attack. The leaching process was effective in the removal of heavy metals, and in some cases, the removal of substantial amounts of ash forming components. Significant changes in the calorific value and the volatile matter concentration have not been observed. The pyrite removal is a selective process in which the coal matrix remains intact. Direct contact between cells and pyrite appears to be essential. Optical image analysis in combination with the texture analysis system demonstrated that the pyrite particles completely enclosed in the carbon matrix are not accessible to microbial attack [6]. The removal of organic sulphur compounds has not been observed.

One should be aware of the undesirability of the formation of jarosite-like precipitates. Jarosites (basic ferric sulphates) will precipitate if the pH and the ionic strength of the process fluid exceed certain values. Roughly it can be stated that jarosites will precipitate if the ferric iron concentration at pH 1.0 exceeds 14 g/L and at pH 2.0 1 g/L. These precipitates will contribute to the sulphur emissions during the coal combustion as they decompose at temperatures below 700 C. Problems with jarosites have been neglected in most studies, which focused mainly on the pyritic sulphur compounds of the coals, while iron-containing sulphates were not measured.

KINETIC STUDIES

For effective pyrite removal, biomass limitation should be prevented. For that reason the kinetics of pyrite removal and the kinetics of bacterial growth in coal water suspensions have been studied.

The study of the kinetics of pyrite removal is simple. The ferric iron concentration in the process fluid should be followed as a function of time. The kinetics of pyrite removal appeared to be first order in the concentration of pyrite present; 90% pyrite removal can be obtained within 8 to 10 days with coal samples with a particle size distribution ($< 100 \mu\text{m}$) meeting the requirements of installations using powdered coal. Slurry percentages up to 20% do not affect the first order kinetics.

The study of the growth kinetics in leaching processes is more problematical. A reliable direct biomass determination is not available. It has been possible to measure both the kinetics of growth and of pyrite oxidation during the leaching of coal in a 10 L batch fermentor. This was done by analyzing the carbon dioxide and oxygen concentrations as functions of time in the incoming and outgoing air flows [8,9]. A specific growth rate of 0.05 h^{-1} has been observed.

As a consequence of these kinetic studies, a reactor configuration consisting of a mixed flow followed by a plug flow appears to be optimal for a continuous process. The residence time in the first part is determined by the growth rate of the pyrite oxidizing microflora. In this mixed flow reactor, the fresh, incoming coal would be inoculated by intensive contact with coal particles which already have adsorbed biomass. In the plug flow section, the first order kinetics will be exploited in the most efficient way. The use of plug flow alone would result in a washout of biomass. Because epifluorescence microscopy reveals that the cell material is adsorbed almost completely to the solid particles ($>99\%$), recirculation of the process fluid would not result in an effective inoculation of the fresh coal. Kinetic studies also demonstrated that in a mixed flow reactor, the pH should be controlled at 1.8 because at lower pH values, the growth rate diminishes. In the plug flow reactor the pH can drop to lower values. The kinetics of the pyrite oxidation are not influenced by pH values down to about 1.4 [2].

STUDIES ON OXYGEN MASS TRANSFER, MIXING AND SEDIMENTATION IN PACHUCA TANK REACTORS

In order to complete a reactor design which will meet the requirements for oxygen supply and mixing, the following strategy was followed. First a regime analysis was performed in order to identify the relevant mechanisms. Then additional information on the parameters governing oxygen transfer, bulk mixing and sedimentation of solid particles in Pachuca tank reactors was collected. Subsequently, the oxygen consumption rate in an installation fed by a low sulphur coal was calculated using the kinetic data on microbial growth and pyrite oxidation. For these calculations, a reactor configuration consisting of a cascade of Pachuca tank reactors in series has been assumed. The first vessel functions as the mixed flow reactor, the series of the others approximate the plug flow part. From this it was possible to calculate the aeration rate needed to supply enough oxygen in each tank. Finally it was checked whether these aeration rates were high enough to provide appropriate bulk mixing and to prevent accumulation of solid materials in the reactor system.

Regime analysis

From the regime analysis, of which more details are given elsewhere [2,10], the following conditions for the characteristic times for microbial oxygen con-

sumption (t_{OCR}), oxygen mass transfer (t_{OTR}), bulk mixing in the reactor (t_{m}) and sedimentation (t_{s}) have been derived.

$$t_{\text{OTR}} < t_{\text{OCR}} \quad (1)$$

$$t_{\text{m}} < t_{\text{OTR}} \quad (2)$$

$$t_{\text{m}} < t_{\text{s}} \quad (3)$$

Condition 1 is derived from the requirement that an overall depletion of oxygen should be prevented. Condition 2 indicates that local oxygen depletion in the reactor must also be prevented. Condition 3 comes from the requirement that sedimentation should be avoided.

Oxygen transfer

Oxygen transfer has been studied by using oxygen electrodes according to the method of Alvarez-Cuenca and Nerenberg [11]. Measurements of k_1a with varying superficial aeration rates (v_g) have been made in Pachuca tanks filled with water, or with 20% coal in water mixtures. They have led to the following correlation:

$$k_1a = 0.6 v_g \quad (4)$$

t_{OTR} is the reciprocal value of k_1a (for more details see Bos et al. [2]).

Mixing

Mixing time measurements have been performed using the pH method described by Einsele [12]. These measurements have led to the following correlation:

$$t_{\text{m}} = 7.5 [T^2 / v_g g]^{1/3} \quad (5)$$

Sedimentation

Figure 1 gives a schematic overview of the behaviour of the coal in water suspension in the cone of a Pachuca tank. The following phenomena are depicted: settling (1), gliding (2), whirling up (3) and bulk mixing (4). It should be noted that if the Pachuca tanks function in the proper way, the bulk of the suspension is mixed homogeneously. Transport of solid particles by bulk flow is much faster than the settling rate. Settling only takes place in the laminar boundary layer which lines the surface of the cone. Due to gravity, sedimented solid particles glide to the lowest point of the cone and will accumulate there if not removed by the air flow. If the reactor is aerated adequately, the solid particles will be carried in the wake of the rising air bubbles to the region

Fig. 1. Schematic presentation of the various mechanisms involved in sedimentation and suspending of solid particles in a Pachuca tank.

above the laminar boundary layer. If the solid particles reach this region, they will be transported by bulk flow. As regards the sedimentation mechanisms, consisting of the settling in the laminar boundary layer and the gliding down of the particles to the air inlet, the settling in the laminar boundary layer is rate-limiting. Of the suspending mechanisms, the transport of the particles in the wake of the air bubble is the slowest. For this reason, and to prevent the accumulation of solid materials at the bottom of the reactor system, the following condition must be met:

$$\text{flux}_{\text{sedimentation}} = \text{flux}_{\text{whirling up}} \quad (6)$$

$$\text{OR } v_{\text{settling}} \epsilon_{\text{susp}} A_t = Q_g \epsilon_{\text{sed}} \frac{V_{\text{wake}}}{V_{\text{bubble}}} \quad (7)$$

$$\text{OR } v_g = \frac{v_{\text{settling}} \epsilon_{\text{susp}}}{\sigma \epsilon_{\text{sed}}} \cdot \frac{V_{\text{bubble}}}{V_{\text{wake}}} \quad (8)$$

Experiments revealed that, for relatively high gas flows, the efficiency factor σ ranges from 0.3 to 0.4. A conservative value is 0.3. According to Kumar and Kuloor [13] the ratio $V_{\text{wake}}/V_{\text{bubble}} = 11/16$. Using the equation of Richardson and Zaki [14], the settling velocity can be calculated. If the ϵ_{susp} and ϵ_{sed} are known, the superficial gas velocity (v_g) required to prevent accumulation of particles on the bottom of the tank can be calculated from eqn. 8.

CALCULATIONS

The microflora present in an installation processing 100,000 metric ton coal/year has an oxygen consumption of 0.0267 kg/s, if the coal has a pyritic sulphur

content of 0.5% and 90% pyrite removal within 9 days. In a cascade of 10 Pachuca tanks, the oxygen consumption varies from 0.00624 kg/s in the first to 0.00080 kg/s in the last tank. Taking into account the size of the reactors and the k_1a , the superficial aeration rate (v_g) must vary between 0.02 m/s in the first and 0.0025 m/s in the last Pachuca tank. These v_g values are always higher than required for a proper mixing and to prevent settling of solid particles on the bottom of the leaching tanks.

COST ANALYSIS

Recently, Bos et al. [2] published a rather detailed process scheme. This design has been adopted by ESTS BV IJmuiden, The Netherlands, to calculate the cost of the process. From these calculations, it appears that the microbial desulphurization of coal is a realistic option, when the price is compared with

TABLE 1

Investment costs in Dutch guilders for an installation processing 100,000 tons coal, containing 0.5% pyritic sulphur, per year [2]¹

	Low estimate	High estimate
Concrete leaching reactors	6,000,000	6,000,000
Other apparatus	2,700,000	2,700,000
Pipelines and appendages	400,000	400,000
Electric installation and instruments	900,000	900,000
Engineering and assembling	1,000,000	2,400,000
Unforeseen		2,600,000
Total	11,000,000	15,000,000

¹Within the residence time of 9 days, 90% of the pyrite present will be removed.

TABLE 2

Operational costs of a 100,000 tons/year installation [2]

	Low estimate	High estimate
Interest and depreciation	1,600,000	2,600,000
Water and chemicals	150,000	225,000
Electric power (8500 h 400–500 kW)	580,000	725,000
Maintenance	170,000	750,000
Cost of labour (4 shifts of 5–6 workers)	1,500,000	1,800,000
Total	4,000,000	6,100,000

Costs per ton of coal varies between Dfl. 40 and 61. Costs include milling.

TABLE 3

Operational costs of 1,000,000 tons/year installation, based on investment costs which are $5\times$ of that of the 100,000 tons/year installation [2]

	Low estimate	High estimate
Interest and depreciation	8,000,000	13,200,000
Water and chemicals	1,500,000	2,250,000
Electricity	2,890,000	7,250,000
Maintenance	850,000	3,750,000
Costs of labour	3,000,000	3,600,000
Total	16,240,000	30,050,000

Cost price per ton of coal varies between Dfs 17 and 30.

other sulphur-removing techniques. Treatment of 1 metric ton of coal in a 1,000,000 metric ton coal per year installation would cost between Dfl. 17 and Dfl. 30 ($\$1 \approx 2$ Dfl.). Details of the cost analysis are given in Tables 1, 2 and 3.

DISCUSSION

The data reviewed and presented in the foregoing demonstrate that microbial desulphurization is technically feasible. The cost analysis suggests that microbial desulphurization is competitive to other sulphur reducing techniques. Whether the process can be realized depends on the coal types available, the local situation and governmental standards and regulations.

The prospects of using coal cleaning techniques such as HGMS, ESS and microbial desulphurization of coal, in Dutch industry, have been discussed by van Steenberg [15]. Due to the selective removal of inorganic sulphur compounds and heavy metals without considerable carbon losses, the microbial desulphurization process is superior to the other physical separation techniques. In the physical processes, effective removal of pyrite is always combined with a high percentage of carbon losses. Only if the coals are milled to extremely fine particles can the effect be improved. However, van Steenberg is pessimistic about the possible application of microbial coal desulphurization in Dutch industry. Public concern about the effects of acid rain has forced the Dutch government to make the standard for the maximal percentage of sulphur that can be accepted in coals more stringent. After 1990, this standard will be lowered to a maximum of 0.35% for coals that are burned without the application of any sulphur binding technique during or after burning. For this reason, only coals with an organic sulphur content of less than 0.35% are suitable for a microbial desulphurization process, because in the Dutch study the removal of organic sulphur compounds has not been observed. These coals are rare.

However, in the literature, reports can be found suggesting that organic sulphur compounds can also be removed biologically. This possibility should be checked thoroughly. One of the main problems is a reliable direct determination of organic sulphur in coal. Only an indirect organic sulphur determination is possible. Data are obtained by subtracting pyritic- and sulphate-sulphur from the percentage of total sulphur present. Total sulphur analysis is without problems, but pyritic sulphur analysis appears to be unreliable as has been demonstrated by a round robin analysis organized among several institutes in The Netherlands.

Van Steenberg [15] suggested that the use of pre-cleaned coals might be feasible if they are burned in installations in which lime injection in the flame is used to reduce the sulphur dioxide emission.

He also discussed the possibility of using various techniques as a cleaning step in the preparation of coal water mixtures. However, in his view the potential of the physical and microbiological cleaning techniques to remove ash forming components is too small and preference is given to froth flotation.

One might ask whether the results obtained in the Dutch study, as have been discussed in this paper, are applicable for the development of a process for high pyritic materials, including coal fines and rejects. In cooperation with Bergbau Forschung GmbH of Essen, FRG, and the University of Cagliari in Italy, a research programme has recently been started which is partly funded by the Commission of the European Communities.

From the applied microbiological studies, it appears that the precipitation of jarosite-like compounds must be avoided. When treating low sulphur coals, the process water can be recirculated to a rather high extent without any problems. However, in the treatment of high sulphur coals, the recirculation ratio that can be used must be reduced considerably in order to prevent jarosite precipitation. As a consequence, the use of water will increase. Another possibility for preventing jarosite precipitation is a reduction of the coal concentration. In the Dutch study, a slurry of 20% coal in water has been used. Reduction of the concentration has a clear negative effect on the economics of the process. Although a low pH in the plug flow part of the reactor system will help to reduce the precipitation problem to some extent, one must conclude that the jarosite precipitation will strongly influence the feasibility of the microbial leaching of high sulphur coals.

Another problem connected with the treatment of high sulphur coals might be heat production. Only a small part of the energy produced by the oxidation of pyrite is used for the synthesis of bacterial biomass. Most energy is liberated as heat. Because huge reactor systems will be required the rate of heat dissipation will be low compared with the rate of heat production. Calculations on the equilibrium temperature as a function of the pyritic content and slurry percentage will be published elsewhere. This heat production does not offer any serious problem in the treatment of low sulphur coals in which mesophilic

mixed cultures are used. It is even advantageous in keeping the system at a comfortable temperature for the pyrite oxidizing bacteria with an optimal temperature around 30°C. The use of such mesophilic microbial systems in the treatment of high sulphur coals will offer problems, since cooling of the reactor is clearly unrealistic. An alternative is the application of thermophilic pyrite oxidizers, such as the *Thiobacillus*-like isolates of Norris et al. [16]. These have an optimal operating temperature about 50°C. Or even *Sulfolobus* species with an optimum operating temperature of 70°C can be applied.

The air flow needed for the oxidation of pyrite will increase proportionally with pyrite content in the coal. In the Dutch design for low sulphur coals, the superficial gas velocities in the first part of the reactor system are already rather high. It is not reasonable to expect that if this superficial gas velocity was increased considerably, the oxygen transfer rate would increase proportionally. If high sulphur coals are to be treated in Pachuca tank reactors, one must expect oxygen limitation in the first part of the reactor system. Modification in the reactor design (e.g. draft tubes) might improve oxygen transfer.

The use of high sulphur coals will not substantially affect the bulk mixing phenomena. However, difficulties can be expected from settling phenomena. In high sulphur containing materials, a considerable part of the pyrite is free of the coal matrix and the heavy pyrite particles would settle rather rapidly, especially if one considers the treatment of high sulphur coal fines with a particle size of around 0.5 mm.

In conclusion it can be stated that, compared to the microbial leaching of low sulphur coals, the treatment of high sulphur coals offers some serious problems that only can be solved by further studies.

LIST OF SYMBOLS

a	= specific surface area (m^2/m^3)
A_t	= cross sectional area of the tank (m^2)
g	= acceleration due to gravity (m^2)
H	= height of the reactor (m)
k_1	= mass transfer coefficient (m/s)
T	= diameter of the reactor (m)
t_m	= characteristic mixing time (s)
t_{OCR}	= characteristic oxygen consumption time (s)
t_{OTR}	= characteristic oxygen transfer time (s)
t_s	= characteristic sedimentation time (s)
V_{bubble}	= volume of the air bubble (m^3)
v_g	= superficial gas velocity (m/s)
v_{settling}	= settling velocity (m/s)
V_{wake}	= volume of the wake behind the air bubble (m^3)
ϵ_{sed}	= porosity of the sediment (m^3 particles/ m^3)

ϵ_{susp} = porosity of the suspension (m^3 particles/ m^3)
 σ = ratio between porosity in the wake and the porosity in the sediment.

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REFERENCES

- 1 Zarubina, A.M., Lyalikova, N.N. and Schmuk, E.I., 1959. Investigation of microbial oxidation of coal pyrite. *Izvest. Akad. Nauk SSSR. Otd. Tekh. Nauk, Met. Topl.*, 1: 117-119 (in Russian).
- 2 Bos, P., Huber, T.F., Kos, C.H., Ras, C. and Kuenen, J.G., 1986. A Dutch feasibility study on microbial coal desulphurization. In: R.W. Lawrence, R.M.R. Brannion, and H.G. Ebner (Eds.), *Fundamental and applied biohydrometallurgy. Proc. Sixth Int. Symp. on Biohydrometallurgy*, Vancouver, B.C. Canada, Elsevier, Amsterdam, pp. 129-150.
- 3 Doddema, H.J., 1983. Partial microbial oxidation of pyrite in coal followed by oil agglomeration. In: G. Rossi and A.E. Torma (Eds.), *Recent progress in biohydrometallurgy. Associazione Mineraria Sarda*, Cagliari, Italy, pp. 467-478.
- 4 Detz, C.M. and Barvinchak, G., 1979. Microbial desulfurization of coal. *Min. Congr. J.*, 65: 75-86.
- 5 Bos, P., Vleeskens, J.M., Kos, C.H. and Hamburg, G., 1987. Microbial desulphurization of coal: Characterization of the products. In: J.A. Moulijn, K.A. Nater and H.A.G. Chermin (Eds.), *Coal science and technology, Vol. 11, 1987 Int. Conf. on Coal Science*, Maastricht, The Netherlands, Elsevier, Amsterdam, pp. 431-434.
- 6 Vleeskens, J.M., Bos, P., Kos, C.H. and Roos, M., 1985. Pyrite association and coal cleaning: An optical image analysis study. *Fuel*, 64: 342-347.
- 7 Lamont, A.G.N., 1958. Air agitation and Pachuca tanks. *Can. J. Chem. Eng.*, 36: 153-160.
- 8 Huber, T.F., Kossen, N.W.F., Bos, P. and Kuenen, J.G., 1983. Modelling, design and scale up of a reactor for microbial desulphurization of coal. In: G. Rossi and A.E. Torma (Eds.), *Recent progress in biohydrometallurgy. Associazione Mineraria Sarda*, Cagliari, Italy, pp. 279-289.
- 9 Huber, T.F., Ras, C. and Kossen, N.W.F., 1984. Design and scale up of a reactor for the microbial desulphurization of coal: A kinetic model for microbial growth and pyrite oxidation. In: *Proc. Third European Conf. on Biotechnology, Vol. III, München*, pp. 151-159.
- 10 Huber, T.F., Kossen, N.W.F., Bos, P. and Kuenen, J.G., 1984. Design and scale up of a reactor for microbial desulphurization of coal: A regime analysis. In: E.H. Houwink and R.R. van der Meer (Eds.), *Innovations in biotechnology: Progress in industrial microbiology, Vol. 20*, Elsevier, Amsterdam, pp. 179-189.
- 11 Alvarez-Cuenca, M. and Nerenberg, M.A., 1981. The plug flow model for mass transfer in three-phase fluidized beds and bubble columns. *Can. J. Chem. Eng.*, 59: 739-745.
- 12 Einsele, A., 1976. Charakterisierung von Bioreaktoren durch Mischzeiten. *Chem. Rundschau*, 29: 53-55.

- 13 Kumar, R. and Kuloor, N.R., 1970. The formation of bubbles and drops. *Adv. Chem. Eng.*, 8: 255-368.
- 14 Richardson, J.F. and Zaki, W.N., 1954. Sedimentation and fluidization: Part 1. *Trans. Inst. Chem. Eng.*, 32: 35-53.
- 15 Steenbergen, H.B. van, 1985. Eindrapport technisch-economische evaluatie project steenkoolzuivering. Inschatting van de vooruitzichten van voorgereinigde kool in de Nederlandse industrie. ESTS BV, IJmuiden.
- 16 Norris, P.R., Brierley, J.A. and Kelly, D.P., 1980. Physiological characteristics of two facultatively thermophilic mineral-oxidizing bacteria. *FEMS Microbiol. Lett.*, 7: 119-122.