DESIGN AND SCALE UP OF A REACTOR FOR MICROBIAL DESULPHURIZATION OF COAL: A REGIME ANALYSIS

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ABSTRACT

As a part of the procedure to design and scale-up a reactor for the microbial desulphurization of coal, a regime analysis is presented. Experimental data on the kinetics of the microbial desulphurization of coal are presented as characteristic times.

To optimize the reactor configuration the characteristic times for bacterial growth (t\textsubscript{growth} = 1/\mu = 1 day) and pyrite oxidation (t\textsubscript{reaction} = 1/k = 4 days) are compared. It was concluded that an optimal reactor configuration consists of a mixed flow reactor with a residence time of 1 day to prevent wash out of biomass. The mixed flow reactor is followed by a plug flow reactor. Over 90% pyrite removal can be obtained using this configuration with an overall residence time of 9 days. From a practical point of view, a cascade of 10 mixed flow reactors is a reasonable configuration which would give 90% pyrite removal in 11 days.

To formulate criteria for oxygen mass transfer and bulk mixing, the oxygen consumption time has been determined. To avoid overall or localized oxygen exhaustion, the mixing time (tmix) and the oxygen transfer time from the gas phase to the liquid phase (t\textsubscript{G/L} = 1/k\textsubscript{a}) must both be smaller than the oxygen consumption time (t\textsubscript{O2}). When desulphurization proceeds, t\textsubscript{O2} increases from 0.6 hour in the mixed flow reactor to 5 hour at the outlet of the plug flow reactor.

INTRODUCTION

In order to facilitate the reintroduction of coal as an energy source in the Netherlands, an extensive research program (NOK) which aims at the inventariation of the technical and economical consequences of the enhanced use of coal as an energy source has been started.

One major environmental drawback would be an increase in sulphur dioxide emission due to the presence of finely dispersed sulphidic minerals in the coal. The objective of our research is therefore to investigate the technical and economical feasibility of microbial desulphurization of coal before combustion. Detz and Barvinchak (ref. 1) published a feasibility study in which they concluded, that microbial desulphurization of coal can compete successfully with chemical coal desulphurization techniques and stack gas desulphurization. In
their study the attention paid to process and reactor design and scale up was limited.

During the microbial desulphurization of coal, the insoluble sulphidic minerals, mainly pyrite (FeS₂), are oxidized to ferric iron and sulphates which are far more soluble.

\[ 4 \text{FeS}_2 + 15 \text{O}_2 + 6 \text{H}_2\text{O} \rightarrow 4 \text{Fe}^{3+} + 8 \text{SO}_4^{2-} + 4 \text{H}_3\text{O}^+ \]

In an aquatic environment this reaction is effectively catalysed by a mixed culture in which the autotrophic microorganism *Thiobacillus ferroxidans* predominates (1-5). Direct contact between the cells and the mineral seems to be essential for catalytic activity (ref. 5, 6). In order to make the pyrite surface accessible to the microorganisms, pulverization of the coal is necessary. Grinding to a particle size used in commercial powder coal burners (< 100 μm) suffices (ref. 3, 4, 7). From the literature one might conclude that the optimal temperature ranges from 20 °C to 35 °C and the optimum pH from 1.8 to 2.5 (ref. 2-4, 6, 7). In order to supply oxygen and carbon dioxide, aeration of the suspension is needed. Pyrite oxidation apparently follows first order kinetics with respect to the pyrite surface area (ref. 3).

At slurry densities up to 20 %v % coal the first order rate constant is not influenced (ref. 9).

A lot of experimental work has been done in shake flasks, where the leaching behaviour of various coal samples employing pure cultures as well as mixed cultures was investigated (ref. 1-4, 7, 8). From this work, a general impression of the kinetics of microbial leaching can be obtained, but because most experiments were not "design orientated" a lack of the information needed for engineering purposes still exists. For example, data on microbial growth rates are rather scarce. For a proper feasibility study, a detailed process and reactor design is a necessity. Therefore, our research is initially focussed on this design and attention is also be paid to scaling up. Experiments were carried out to obtain additional kinetic data.

Our research program has reached the point where enough information has been obtained with respect to the kinetics of pyrite oxidation and bacterial growth to reach conclusions in process design and to specify the requirements which a reactor design should meet. To these purposes the scale-up procedure, as proposed by Oosterhuis and Kossen (10), has been adapted (Fig. 1).
FIGURE 1.
Procedure for Design and Scale-Up

Provisional design based on literature data

| Tracing rate limiting processes: regime-analysis |
| Scale-down of the rate limiting processes |
| Investigation laboratory scale of the rate limiting processes |
| | Optimizing laboratory scale of the rate limiting processes |

| Final design |

No data are available on microbial desulfurization of coal on a commercial scale. For this reason, the provisional design is based on the available literature data and rough estimates derived from first principles. Due to the small size of the coal particles, fluid bed reactors and packed bed reactors are impractical because of the small settling velocity respectively the high pressure drop to be expected. Therefore external aeration of a recirculating liquid flow combined with a liquid/solid reactor is also not applicable. The feasible reactor type turned out to be an aerated slurry reactor. This implies that a separate settler is needed of dewatering of the cleaned coal is necessary.

As discussed before (11), in reactor design a compromise must be found between mixed flow and plug flow. On one hand backmixing is needed to prevent washout of biomass, but on the other hand, because of the first order kinetics, a plug flow character is desirable. As a compromise, a cascade of mixed flow reactors has been chosen in the provisional design. (also see fig. 2).

With respect to the choice of a mixing device, it was concluded that gas agitation is preferable to mechanical agitation. This conclusion is based on the following considerations:

- A coal suspension of pH 1.8 - 2.5 is rather corrosive.
  Therefore moving parts should be avoided if possible.

- The scale of a commercial installation will be large.

- In the case of a power failure the suspension will settle.
  Resuspension in a gas agitated reactor is easier then in a mechanically agitated reactor, as reported by Kipke (ref. 12).

This paper reports on the regime analysis performed on the provisional design (see fig. 1) and based on a further extension and interpretation of previously published results (11). At first a theoretical background of the reactor system
under study is discussed and then the kinetic data needed to reach conclusions are presented. Also experimental methods are discussed briefly.

REGIME ANALYSIS

The regime analysis is performed to develop criteria for design. A design which maintains optimal conditions for the microorganisms everywhere in the reactor with respect to pyrite oxidation is aimed for. The reactor volume will then be minimized.

In general regime analysis can be based on the calculation of characteristic lengths, characteristic velocities and characteristic times. The latter is common practice in biotechnology (ref. 10).

For optimal design of a bioreactor two major conditions must be met:

- The prevention of biomass limitation (lack of catalyst).
  In this case the amount of biomass must be sufficient to cover the pyrite surface area to a maximum extent (ref. 12).

- The environment of the microorganisms must be optimal for pyrite oxidation. This condition does not necessarily imply conditions optimal for microbial growth.

The starting point of a regime analysis is the knowledge of the kinetics of the microorganisms involved. Data on micro kinetics are not dependent on the reactor system and therefore can be used to develop design criteria.
Biomass limitation

As already mentioned in the introduction a compromise must be found between plug flow and mixed flow behaviour (Ref. 11). Mixed flow is favourable with respect to the production of biomass and the prevention of washout. However plug flow results at a given conversion, in a smaller reactor volume, if biomass limitation can be avoided. Therefore a reactor configuration should be employed consisting of a mixed flow reactor, to generate a sufficient amount of biomass, followed by a plug flow reactor fed with a suspension containing enough biomass.

To avoid washout of biomass, the dilution rate in the mixed flow reactor must be lower than the growth rate. This condition can be expressed in characteristic times as follows:

\[ t_{\text{res}}\left(=\frac{1}{D}\right) > t_{\text{growth}}\left(=\frac{1}{\mu}\right) \]

The relative sizes of the mixed flow and plug flow reactors are governed by the relationship between the bacterial growth rate and the reaction rate (pyrite oxidation rate). The following regimes can be distinguished:

1. The growth rate is large compared with the reaction rate:

\[ t_{\text{growth}}\left(=\frac{1}{\mu}\right) < t_{\text{reaction}}\left(=\frac{1}{k}\right) \]

In this situation, a small mixed flow reactor is sufficient to produce enough biomass, thus the overall reactor volume is determined by the pyrite oxidation rate. The large proportion of the entire reactor volume taken up by the plug flow reactor results in an approximation of plug flow behaviour overall. Due to the first order kinetics reactor volume as a whole is minimized.

2. The growth rate is small compared with the reaction rate:

\[ t_{\text{growth}}\left(=\frac{1}{\mu}\right) > t_{\text{reaction}}\left(=\frac{1}{k}\right) \]

In this situation the major problem is shortage of biomass. Bacterial growth is enhanced by carrying out the process in one mixed flow reactor because of the autocatalytic nature of biocatalysed reactions. In theory, a plug flow reactor with recycling of biomass would result in a smaller reactor volume, but in this system separation of biomass from the coal suspension is impossible or at least very troublesome.

Optimal environment for the microorganisms

The major points of interest in providing an optimal environment for the microorganisms to catalyse the pyrite oxidation are the prevention of oxygen depletion anywhere in the reactor and the prevention of settling of the suspension.

The phenomena involved in the transport of oxygen from the gas phase to the
microorganisms are shown schematically in fig. 2.

![Diagram](image)

Fig. 2. Scheme showing oxygen transport through the reactor.

These phenomena can be expressed in characteristic times as follows:

- Mass transfer from gas phase to liquid phase: $t_{G/L} = 1/k_{1a}$
- Mixing of the liquid/solid suspension to prevent localized oxygen depletion in not directly aerated regions: $t_{mix} = V_r/β_1$
- Oxygen consumption by microorganisms: $t_{OUR} = C_{O_2}/r_0$

Also, we can formulate a characteristic time for settling of the suspension:

- Settling time: $t_{sett} = H/v_{sett}$

Shortage in the reactor as a whole will occur if the oxygen consumption by the microorganisms is faster than oxygen transfer from the gas phase to the liquid phase. To prevent this overall oxygen limitation, the following condition should be met:

$$t_{G/L} < t_{OUR}$$

Usually oxygen transfer from the gas phase to the liquid phase is not uniformly distributed through the reactor. In an oxygen-consuming system, oxygen gradients will exist. These gradients are leveled off by bulk mixing. Local oxygen exhaustion occurs if oxygen transport by bulk mixing is slower than local oxygen consumption. This results in the condition:

$$t_{mix} < t_{OUR}$$

Closely related to this mixing criterion is the need for maintaining all particles in suspension. Obviously, in a bed of settled particles oxygen transport by bulk mixing is almost absent. The criterion for suspending particles can be expressed as:

$$t_{mix} < t_{sett}$$

Hereby the comparison of characteristic velocities might be more convenient to give insight into the phenomena of interest:

$$v_{sett} < v_L$$
DETERMINATION OF CHARACTERISTIC TIMES

Time for bacterial growth

The bacterial growth rate was determined in a 10-L batch reactor, as reported before (11). The growth rate was determined by measuring the oxygen and carbon dioxide uptake rates by gas phase analysis. In the beginning of the batch experiment, during the exponential growth phase, the oxygen uptake rate resulting from pyrite oxidation, increased proportionally to the carbon dioxide uptake rate, which was related to the formation of new biomass. During this period the growth rate was found to be:

\[ \mu = 1 \text{ day}^{-1} \]

Reaction time

Most authors (ref. 3, 9) tend to describe microbial oxidation of pyrite by first order kinetics related to the amount of available surface area. Others (4) suggest first order kinetics related to the pyrite concentration. Although from a mechanistic point of view the surface area approach seems to be more likely, for the purposes of regime analysis a description based on pyrite concentration is accurate enough and less complicated.

This pyrite conversion can be described by the relation:

\[ r_{\text{FeS}_2} = -k \cdot C_{\text{FeS}_2} \]

The reaction rate constant \( k \) was determined in repeated fed-batch experiments. At fixed time intervals (1 day), a portion of the reactor contents was removed and replaced by fresh suspension. In this manner a cascade of three repeated bed batch reactors was used. The suspension removed from the first reactor was used as feed for the second reactor and the product of the second reactor was used as feed for the third one. The conversion reached in each reactor was determined. From these data the reaction rate constant was calculated. Experimental design and detailed results will be published elsewhere. The reaction rate constant proved to be:

\[ k = 0.25 \text{ day}^{-1} \]

In the literature experimental data from batch experiments in shake flasks are usually presented as the percentage pyrite removal as a function of the exposed time (ref. 2, 3, 7). Although a considerable spread in the results is present, an average value of 90% pyrite removal in 10 days can be used. The reaction rate constant calculated from this data corresponds with our own results. The characteristic time for the reaction is:

\[ t_{\text{reaction}} = \frac{1}{k} = 4 \text{ days}. \]
Oxygen consumption time

The rate of oxygen consumption depends on the pyrite concentration. The time span in which the oxygen present in the suspension is consumed is related to the solubility of oxygen in the suspension and the pyrite concentration. The oxygen consumption time can be defined as follows:

\[
\frac{t_{OUR}}{r_0} = \frac{\frac{Y_{OS} \cdot C_{O_2}^{\#}}{k \cdot C_{FeS_2}}}{C_{O_2}^{\#}} \quad (Y_{OS} = 1 \text{ kg}O_2/\text{kg}FeS_2)
\]

The solubility of oxygen in the coal suspension was determined experimentally. In a 10-L vessel, air was sparged through the suspension until saturation was reached. Subsequently nitrogen was sparged through. The oxygen concentration in the gas flow leaving the vessel was measured until almost zero concentration was reached. The amount of oxygen present in the suspension after saturation with air was calculated by integrating the product of oxygen concentration and gas flow rate versus time. At 30 °C an oxygen solubility of 14 g/m³ was found for a suspension containing 20 w/v powder coal 501 GB 28 supplied by the Dutch Centre for Coal Specimens, Eygelshoven, the Netherlands.

As the desulphurization process proceeds, the pyrite concentration decreases and the oxygen consumption time therefore increases. If, as discussed later, the selected reactor configuration consists of a mixed flow reactor with a residence time of 1 day followed by a plug flow reactor, the following \( t_{OUR} \) can be expected:

- Mixed flow reactor \( : t_{OUR} = 0.6 \text{ hour} \quad (C_{FeS_2} = 2.4 \text{ kg/m}^3) \)
- Outlet plug flow reactor \( : t_{OUR} = 5 \text{ hour} \quad (C_{FeS_2} = 0.3 \text{ kg/m}^3) \)

Settling time

A rough indication of the settling velocity of a dense suspension can be obtained by applying the correlation of Richardson and Zaki(14):

\[
V_{sett.} = V_{sett.}^* e^{-n}
\]

For a coal particle of 100 μm, density 1400 kg/m³ the settling velocity is \(2 \times 10^{-3}\) m/s. For a slurry density of 20 w/v % coal the settling velocity of the suspension is about \(1 \times 10^{-3}\) m/s. Assuming a reactor height of 10 m the characteristic time for settling can be estimated as follows:

\[
\frac{t_{sett.}}{H/V_{sett.}^*} = 3 \text{ hour.}
\]
DISCUSSION

The results of the regime analysis indicate that, with respect to the prevention of biomass limitation, maintaining a sufficient biomass concentration will not be troublesome because the growth time \((1/\mu)\) of the biomass is much smaller than the reaction time \((1/k)\). A small mixed flow reactor \((t_{\text{res}} = 1\ \text{day})\) is sufficient to produce enough biomass to prevent washout. If the mixed flow reactor is followed by a plug flow reactor, a minimal reactor volume is obtained.

The residence time required to reach a certain conversion can be calculated as follows (ref. 15):

\[
\begin{align*}
\text{Mixed flow reactor} & : \frac{C}{C_0} = (k \cdot t_{\text{res}} + 1)^{-1} \\
\text{Plug flow reactor} & : \frac{C}{C_0} = \exp(-k \cdot t_{\text{res}}) \\
\text{Cascade of } N \text{ mixed flow reactors} & : \frac{C}{C_0} = \left(1 + \frac{k \cdot t_{\text{res}}}{N} \right)^{-N} 
\end{align*}
\]

This reactor configuration should be compared with the reactor configuration suggested in the provisional design (a cascade of 3 mixed flow reactors). As a third possible reactor configuration, a cascade of 10 mixed flow reactors has been considered. In order to compare these reactor configurations the overall residence time needed for 90% pyrite removal was calculated.

\[
\begin{align*}
\text{Mixed flow reactor followed} & : t_{\text{res}} = 9\ \text{days} \\
\text{plug flow reactor} & \\
\text{Cascade 3 mixed flow reactors} & : t_{\text{res}} = 13\ \text{days} \\
\text{Cascade 10 mixed flow reactors} & : t_{\text{res}} = 11\ \text{days} 
\end{align*}
\]

Thus in the provisional reactor design, a 40% longer residence time is needed. A cascade of 10 mixed flow reactors in series presents a reasonable compromise. The large number of reactors in series seems to be impracticable, but it should be kept in mind that the overall reactor volume required is rather large. Therefore, to reduce the size of each separate reactor, a large number of reactors must be necessary.

The overall reactor volume of a 10 reactor cascade to treat 100,000 tons of coal per year at a slurry density of 20 w/v % coal would be:

\[ V = 16,500\ \text{m}^3. \]

As oxygen consumption time varies during desulphurization, the requirements for mixing and mass transfer will also vary. On the other hand the requirements to prevent settling of the suspension are constant throughout the reactor. Because the characteristic time for settling lies within the range of oxygen consumption times, in determining the mixing requirements both oxygen transfer and suspending characteristics should be considered.
CONCLUSIONS

1. Biomass limitation is avoided by employing a mixed flow reactor with a residence time of at least 1 day at the beginning of the process.
2. The reactor configuration of the provisional design involves a 40% longer residence time. From a practical point of view, a cascade of 10 reactors seems to be a reasonable compromise.
3. The reactor configuration requiring the lowest overall residence time consists of a mixed flow reactor \((t_{\text{res}} = 1\) day) followed by a plug flow reactor. A 90% pyrite removal can be obtained at an overall residence time of 9 days.
4. The oxygen consumption time varies when the desulphurization process proceeds. For this reason the mixing and mass transfer requirements also vary.
5. The characteristic time for settling of the suspension is of the same order of magnitude as the mixing time required for bulk mixing. Therefore the prevention of settling has also to be considered.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>(C_{O2})</td>
<td>Oxygen concentration in the suspension</td>
<td>(\text{kg.m}^{-3})</td>
</tr>
<tr>
<td>(C_{FeS2})</td>
<td>Pyrite concentration in the suspension</td>
<td>(\text{kg.m}^{-3})</td>
</tr>
<tr>
<td>(D)</td>
<td>Dilution rate</td>
<td>(\text{day}^{-1})</td>
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<tr>
<td>(H)</td>
<td>Height of the reactor</td>
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<td>(k)</td>
<td>First order reaction rate constant</td>
<td>(\text{day}^{-1})</td>
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<tr>
<td>(k_{va})</td>
<td>Volumetric mass transfer coefficient</td>
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<tr>
<td>(n)</td>
<td>Constant in correlation Richardson and Zaki</td>
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<tr>
<td>(r_0)</td>
<td>Oxygen consumption rate</td>
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<td>Characteristic velocity settling particles</td>
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<td>Settling velocity particle according to Stokes law</td>
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<tr>
<td>(\mu)</td>
<td>Growth rate</td>
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