Geochemistry of sulfides in coal and microbial leaching experiments.

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Introduction

It is generally acknowledged that micro-organisms have an essential catalytic function in reduction and oxidation reactions which proceed during the cycling of elements in the upper layer of the lithosphere. In the case of sulfur there is overwhelming evidence for microbial activity in the reduction of sulfur species to hydrogen sulfide (H₂S), leading to the precipitation of sulfides, occasionally in the form of sulfide ore deposits. In turn the sulfides can be oxidized by bacteria, whereby the ores are rendered soluble. The latter process has gained interest, because it has proven to be successful in the recovery of metals from otherwise low-grade ores.

By far the most common sulfide in rocks is pyrite (FeS₂). It is an almost omnipresent constituent of coal and deserves our attention as the major source of sulfur, in addition to the organic sulfur constituent. Another environmental aspect of sulfides is that they may accomodate a major part of certain trace elements in coal, which are hazardous when released in the biosphere as a result of coal conversion processes. Thus, one field of interest in efforts to minimize environmental problems of coal-utilization is the thorough removal of sulphides from coal. One of the possible methods is a leaching process based on the decomposition of sulfides by microbial oxidation. We studied a number of hard coal samples imported from different countries with respect to the susceptibility to microbial leaching, as part of our research on microbial desulfurization of coal, which include the environmental aspects of spontaneous microbial oxidation during storage and transport.

Origin of sulfides in coal

According to Berner (1971) three factors dominate pyrite formation in sediments: 1. the concentration and reactivity of iron compounds, 2. the
availability of dissolved sulfate required for sulfide production and
3. the concentration of organic compounds, metabolizable by sulfate
reducing bacteria. In coal forming deposits the last factor probably
does not limit the process. Here only the concentration of dissolved
iron and sulfur possibly limits the precipitation of pyrite precursors.
Their deposition as monosulfides, yielding the black colour of organic
rich sediments, has been established in recent environments. During early
diagenesis at high H₂S pressure reaction with elemental sulfur produces
disseminated pyrite, which often displays the characteristic frambooidal
texture, consisting of spherical aggregates of micro-crystals. Pyrite
formed during early diagenesis is generally fixed to the coal.

As the mineralization process of organic matter under anaerobic
conditions preferentially proceeds via sulfate reduction rather than
through methane production, it follows from the high sulfate concentra-
tion in seawater that coal produced in marine environments will have in
general much higher pyrite contents than fresh water coal deposits. In
the latter, the sulfate originating from decomposed organic matter may
become a significant factor in the pyrite producing process.

During diagenesis and early metamorphism a considerable quantity of
water is progressively expelled from the sediment. This liquid, with
additional water of meteoric origin, may act as a strong solvent, in
particular at high salinity. These kinds of hydrothermal fluids, often
over 100°C at a depth of only 2 or 3 km, are known in a number of cases
to precipitate galena (PbS) and sphalerite (ZnS) in addition to abundant
pyrite (Hunor, 1979). Secondary pyrite settled in cleats, partings and
fissures in coal is a common feature, whereas metal sulfides like galena
and sphalerite regularly occur. It is not unlikely that sulfides are
preferentially deposited in coal, since 1. the coalified organic matter
was probably enriched in metals as some organic compounds are able to
sorb metals, which can be extracted by hydrothermal fluids during
diagenesis, 2. high partial H₂S pressure can be expected in coal,
favouring precipitation of sulfides from the fluid.

Table I shows that the sulfides that happen to occur in coal may
accommodate high concentrations of trace elements, most being notorious
because their potential toxicity.
Table I. (adapted after Vaughan and Craig, 1978). Maximum minor
element contents of common metals in ppm unless otherwise stated.

<table>
<thead>
<tr>
<th>Sulfide</th>
<th>Minor Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>Cu, Co and Ni become major elements in solid solution; As 3%; Pb 5000; Sb 700; Ti 340; Se 300; Ag 200; Au 200; Sn 400.</td>
</tr>
<tr>
<td>Marcasite</td>
<td>As 7800; Ti 5300; Pb 200</td>
</tr>
<tr>
<td>Galena</td>
<td>Ag 3%; Sb 3%; Se 1%; As 1%; Cu 3000; Sn 1300; Zn 1000; Ti 1000; Cd 1000.</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>Cu 5%; Cd 4%; Sb 3%; Hg 1%; Sn 1%; In 1%; Ag 1%; As 1%; Ti 5000; Co 3000; Se 900; Ni 300.</td>
</tr>
</tbody>
</table>

**Microbial leaching of sulfides**

The overall effect of microorganisms in leaching processes is the
decomposition by oxidation of poorly soluble metal sulfides, resulting
in more soluble sulfate according to the schematic reaction:

\[
2\text{FeS}_2 + 7\text{H}_2\text{O} + \text{micro-organism} \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{SO}_4 \quad \text{(Olsen et al., 1980)}
\]

In this reaction not only the sulfur part is oxidized to sulfate, but
also the metal ion is oxidized. Of the micro-organisms involved, the
genus Thiobacillus is probably dominant, although in some geologic
environments the thermophilic bacteria Sulfobulbus is active. For applica-
tions in metallurgy - the recovery of metals from low-grade ores or in
measures against unwanted spontaneous oxidation - the investigations are
mainly directed to *T. ferro-oxidans*. This bacteria oxidizes sulfur as well
as ferrous iron. It is supposed that in particular dissolved ferric iron
acts as a strong oxidizing agent according to the reaction:

\[
\text{FeS}_2 + 4\text{Fe}^{3+} \rightarrow 5\text{Fe}^{2+} + S^0 \quad \text{(Olsen et al., 1980)}
\]

Apart from iron sulfide, many other metal sulfides are known to be
decomposed by this reaction (Manchoe, 1979).

Although the optimum growth of *T. ferro-oxidans* is somewhat higher,
this organism thrives in the natural environment at pH 1.5-2. At this
acidity the actual leaching process proceeds at optimal speed. In
commercial leaching processes the optimal acidity is initially created,
but in nature a considerable incubation time is needed before this pH
is reached.
The microbial leaching of sulfides from coal is by no means a new idea: actually T. ferro-oxidans was initially isolated from acid coal mine drainage water by Temple and Colmer (1951) after microbial activity was suspected to cause the acidity of coal drainage water, particularly in the presence of a pyrite-rich coal. It was soon recognized that the acidophilic micro-organisms could be useful in microbial desulfurization of coal (references cited in Olsen et al., 1980).

**Coal-leaching experiments**

Our first experiments were carried out with samples from a commercial low-sulfur hard coal, enriched with 5% pyrite, and using pure strains of T. ferro-oxidans (by courtesy of Lab. voor Microbiologie, L.N.Wageningen) and mixed cultures of acidophilic bacteria, kindly put to our disposal by Dr. P.R. Norris (University of Warwick, England). It soon appeared that better results were obtained by a mixed culture than with pure T. ferro-oxidans: within 3 weeks 1 g of pyrite in a 20% coal slurry was completely dissolved.

Next, we initiated a series of experiments with relatively pyrite rich coals, containing respectively 1 and 3% pyrite. The samples were collected at a coal-washing plant. The installation of this plant showed strong corrosion as a result of cleaning this particular coal, which we considered to be indicative for acidity of the processing water induced by microbial oxidation of the sulfides. The mixed cultures of acidophilic micro-organisms isolated from the drainage at this coal-washery appeared to be very effective in leaching these pyrite-rich coal varieties. In coal samples with a grain size < 0.1 mm more than 85% of the pyrite was dissolved within ten days. In coal crushed to < 3 mm, 60% of the pyrite was dissolved. Like in most of our experiments we used shake flasks and created an initial pH of 2.

From the leaching experiments carried out during this preliminary stage, we learned: 1. mixed cultures of acidophilic micro-organisms are more effective in leaching pyrite present in coal than pure strains of Thiobacilli; 2. a mixed culture isolated from the drainage of a particular coal is very successful in leaching this coal, apparently because the culture is well-adapted; 3. the positive effect of coal size reduction.

The present results were obtained in a reconnaissance study of the
practical scope of microbial desulfurization of commercial hard coal as imported in the Netherlands for electricity production. We used again shake flasks containing 20% coal slurry and kept at 30°C during 21 days. The slurries were inoculated with the mixed culture isolated at the coal-washing plant. A first series of experiments was monitored for sulfate in order to follow the microbial breakdown of pyrite. For in particular the coal samples containing a relative high pyrite content the maximum sulfate concentration was observed after ten days; for samples containing little pyrite the sulfate concentration did not change significantly during the experiment. The second series of experiments served to analyse in more detail the quantity of sulfide dissolved and in addition the coal was investigated for some major and trace elements before and after leaching. The results of the sulfur determinations are compiled in table 2.

Table 2. Desulfurization results of coal. Total sulfur analyzed by W.J. Buiks, FCI-TNO, Zeist; pyritic sulfur analyzed by the first author.

<table>
<thead>
<tr>
<th>Origin and grain size</th>
<th>Treatment</th>
<th>% total sulfur before leaching</th>
<th>% pyritic sulfur before leaching</th>
<th>% total sulfur after leaching</th>
<th>% pyritic sulfur after leaching</th>
<th>% total S leached after leaching</th>
<th>% pyritic S leached after leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poland</td>
<td>before leaching</td>
<td>.68</td>
<td>.19</td>
<td>28</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>.1 mm</td>
<td>after leaching</td>
<td>.62</td>
<td>.16</td>
<td>26</td>
<td>16</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>3 mm</td>
<td>after leaching</td>
<td>.68</td>
<td>.17</td>
<td>25</td>
<td>11</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ruhr</td>
<td>before leaching</td>
<td>.95</td>
<td>.16</td>
<td>17</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>.1 mm</td>
<td>after leaching</td>
<td>.87</td>
<td>.16</td>
<td>18</td>
<td>0</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>3 mm</td>
<td>after leaching</td>
<td>.84</td>
<td>.11</td>
<td>13</td>
<td>31</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Wales</td>
<td>before leaching</td>
<td>1.15</td>
<td>1.62</td>
<td>51</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>.1 mm</td>
<td>after leaching</td>
<td>1.49</td>
<td>.07</td>
<td>5</td>
<td>56</td>
<td>53</td>
<td>53</td>
</tr>
<tr>
<td>3 mm</td>
<td>after leaching</td>
<td>2.38</td>
<td>1.26</td>
<td>53</td>
<td>49</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>U.S.A.</td>
<td>before leaching</td>
<td>.95</td>
<td>.08</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>.1 mm</td>
<td>after leaching</td>
<td>.80</td>
<td>.02</td>
<td>3</td>
<td>75</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>3 mm</td>
<td>after leaching</td>
<td>.76</td>
<td>.03</td>
<td>4</td>
<td>65</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Australia</td>
<td>before leaching</td>
<td>.38</td>
<td>.01</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>.1 mm</td>
<td>after leaching</td>
<td>.36</td>
<td>.00</td>
<td>0</td>
<td>100</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>3 mm</td>
<td>after leaching</td>
<td>.36</td>
<td>.00</td>
<td>0</td>
<td>100</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

It is obvious from table 2 that the amount of pyritic sulfur in the considered coal samples is low with respect to the total sulfur content, except for the Wales coal. The latter is not used for electricity production but for small-scale industrial underfiring. The result of microbial desulfurization applied to the Wales coal was as could be

1) this research was financially supported by the Mins. of Econ. Affairs.
expected from our previous experiments with pyrite-rich coal. The low-sulfur coal from Australia and the coal from the U.S.A. contain small amounts pyritic sulfur, which are effectively dissolved. However, this reduction does not contribute substantially to the total sulfur reduction. The poor results obtained for the Ruhr and the Poland coal is possibly due to the neutralizing effect of solubilized carbonates, since the acidity in these experiments increased to $\text{pH} > 2\frac{1}{2}$ whereas the other experiments exhibited pH values between 2 and 2\frac{1}{2}. The observation that the coarse fraction of the Ruhr coal leached better than the fine fraction, can be explained by inhibitory effects of compounds released in the latter.

Table 3. Effect of leaching on some trace elements in coal < .1 mm.

<table>
<thead>
<tr>
<th>Origin</th>
<th>Concentration before leaching</th>
<th>Removed by leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu ppm</td>
<td>Zn ppm</td>
</tr>
<tr>
<td>Poland</td>
<td>33</td>
<td>4 DTL</td>
</tr>
<tr>
<td>Ruhr</td>
<td>50</td>
<td>8 DTL</td>
</tr>
<tr>
<td>Wales</td>
<td>25</td>
<td>7 DTL</td>
</tr>
<tr>
<td>U.S.A.</td>
<td>26</td>
<td>31</td>
</tr>
<tr>
<td>Australia</td>
<td>15</td>
<td>5 DTL</td>
</tr>
</tbody>
</table>

1) NAA supervised by Dr. H.A. van der Sloot, E.C.N. Petten; 2) AAS of leaching liquid by Dr. J.P.J. van Dalen, Anal. Scheik., TH Delft.

Table 3 illustrates the effect of leaching with respect to some metals representing the group of "chalcopyrite" elements. Although in a large number of cases the concentrations were around detection level (DTL), the figures allow a preliminary conclusion. The leachability of the Wales coal is well reflected by the concentrations determined for the leaching liquid. Considering Cu and Zn the same conclusion is valid for the U.S.A. and the Australian coal, despite of the minute quantities of pyrite present. Although the Ruhr and Poland coal varieties contain more pyrite, less Cu and Zn was found in the leaching liquid. We suppose for the Ruhr and Poland coal that the fraction of pyrite dissolved represent a relative pure pyrite, with low concentrations of trace elements.

References