OPTIMIZATION OF METALLURGICAL PROCESSES USING HIGH RATE BIOTECHNOLOGY

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Abstract

Existing metallurgical operations can be optimized by implementing engineered bioreactor systems in the process configuration. For instance, metals can be recovered safely and economically from process and waste streams using biogenic sulfide.

This paper focuses upon possible applications of high rate biotechnology in metallurgy and mining. Metal recovery from liquid streams (process bleed streams, leach water, waste streams), integrated removal of (fugitive) SO₂, treatment of acid blowdown and other options will be described.

Practical examples are given. A large-scale application of biotechnology at Pasminco’s Budel Zink refinery is described. Here acid plant blowdown is treated together with electrolyte magnesium bleed. Concentrated zinc sulfide (10 tpd) is produced biologically, eliminating the production of gypsum and closing the refinery sulfur cycle.

Recovery of metals from solution at Kovehute Pribram in the Czech Republic is the second practical example. In this case H₂S is produced on-site for metal removal from an alkaline slag dump leachate.

At the Caribou mine in New Brunswick, Canada, acid mine drainage is treated with biogenic sulfide. This plant is situated upstream a lime neutralization plant. As a result, reusable ZnS is produced, the volume of the sludge (gypsum and hydroxides) from the lime plant is reduced by 50%, the sludge is free of heavy metals and the final effluent concentration of heavy metals is in the ppb range. In the second phase of this project, metals will be recovered from stored tailings, resulting in significant revenues.
Introduction

Besides the well known biological oxidation processes used for example in bioleaching applications, more and more processes are being developed in which biological reduction is the key reaction. Anaerobic bacteria are able to reduce oxidized sulfur components and metals to the less oxidized state. These processes can be used to advantage in recovering or removing metals from process streams and/or waste water streams [2, 4, 5, 7, 8]. Very low residual metal concentrations can be reached in the treated streams and simultaneously, sulfate can be removed to less than 200 ppm if required. By applying high rate, engineered reactor systems and determining the most techno-economical process configuration, biological processes can be applied effectively and economically. In many cases the revenues of the metals recovered offset the investment and operational costs.

The patented technologies described in this paper are developed by the Paques company, which has realized some 500 high rate biological treatment plants worldwide. Thirteen industrial plants specially designed for the reduction of sulfur compounds are successfully operated on a continuous basis. The technology is marketed under the THIOPAQ®-trademark.

Graph I: Cumulative number of THIOPAQ® S-reduction applications

H2S production
The group of anaerobic micro-organisms characterized as sulfate reducing bacteria are able to reduce oxidized sulfur components to hydrogen sulfide or H2S. In order to reduce oxidized sulfur components to hydrogen sulfide the bacteria use a substrate, which is oxidized simultaneously. For this purpose organic compounds like ethanol can be used. For large scale applications hydrogen gas is used which is produced on site by reforming natural gas, LPG or naptha [4, 5]. This so-called electron donor or reductant mainly determines the operational costs. The equations for sulfate reduction with ethanol and hydrogen gas are as follows:
3 SO$_4^{2-}$ + 2 C$_2$H$_5$OH $\rightarrow$ 3 HS$^- + 3$ H$_2$O + 3 HCO$_3^-$ + CO$_2$  \hspace{1cm} (1)

SO$_4^{2-}$ + 4 H$_2$ + H$^+$ $\rightarrow$ HS$^- + 4$ H$_2$O \hspace{1cm} (2)

This bio-produced or biogenic H$_2$S can be readily used to precipitate metals from solution.

If removal of sulfate from a liquid stream is not required the cheapest way to produce hydrogen sulfide biologically is the reduction of elemental sulfur [7, 9]. Only 2 electrons are required for the reduction of sulfur to H$_2$S, whereas for sulfate reduction to H$_2$S 8 electrons are needed:

6 S$^{\circ}$ + C$_2$H$_5$OH + 3 H$_2$O $\rightarrow$ 6 H$_2$S + 2 CO$_2$ \hspace{1cm} (3)

Paques developed the THIOPAQ$^\circledR$ BSG (Biogenic Sulfide Generator) process for this purpose. In this case a relatively small bioreactor is fed with an S-feed and a reductant. The produced hydrogen sulfide is stripped from the bioreactor by recycling gas from the bioreactor to a gas/liquid contactor in which the H$_2$S is transferred to the stream to be treated. In this case there is no direct contact between the bacteria and the liquid stream treated.

Instead of feeding the bioreactor with sulfur, local circumstances may favour the use of other oxidized sulfur compounds, such as waste sulfuric acid or SO$_2$.

**H$_2$S utilisation**

The use of H$_2$S generally leads to better metal removal efficiencies and a product which is more compact, stable and re-usable than metal hydroxides or carbonates. Hydrogen sulfide has been used on a large scale to precipitate metals from process water, bleed streams and waste water streams in mining and metallurgical operations. However, traditional sulfide sources (e.g. NaHS and H$_2$S) are expensive and the transport costs per tonne of sulfide are high. Furthermore, the storage and handling of large quantities of sulfide on site calls for extra safety measures. H$_2$S production on site using a chemically catalysed process is only economical at high tonnages.
Using sulfate reducing bacteria, cost-effective and safe H\textsubscript{2}S can be produced on demand and on-site as an attractive alternative to the traditional sources of sulfide [5]. This is outlined further in the case-descriptions for Kovehute and Caribou in this paper.

**Selective metal recovery**

Hydrogen sulfide is used to precipitate heavy metals like copper and zinc to produce their respective metal sulfides, which have a very low solubility [1, 3, 9]. Very low dissolved metal concentrations in the ppb range can be reached for a wide range of metals. Each metal however, has its own pH optimum for precipitation with sulfide. This makes it possible to selectively precipitate different metals at controlled pH stages. For example arsenic, copper and zinc can be recovered selectively at three separate stages each at a different pH.

**Metal reduction**

Some metals however do not precipitate easily as metal sulfides at certain valences. In this case anaerobic bacteria can be used to reduce the metals to a lower valence in order to trigger precipitation. This could be as the metal sulfide but also as metal oxides, carbonates or even as the elemental metal. Examples are selenium, molybdenum and uranium.

**Sulfate removal**

When, besides metals, sulfate has to be removed to low levels the anaerobic biological treatment is followed by a second biological treatment step in which the excess of hydrogen sulfide is oxidized to elemental sulfur [4]:

\[
\text{HS}^- + \frac{1}{2} \text{O}_2 \rightarrow \text{S}^0 + \text{OH}^-
\] (4)

Combined with equation (2), this leads to the overall formula:

\[
\text{H}_2\text{SO}_4 + 4 \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{S}^0 + 5 \text{H}_2\text{O}
\] (5)

It is important to note that by applying this process acidity can be destroyed without the use of alkaline chemicals. This is of particular interest for treatment of waste sulfuric acid or acidic streams containing sulfate and heavy metals, such as Acid Mine Drainage (AMD).

Using this method sulfate can be removed to below 200 ppm, which is far below the 1500 ppm reached in traditional lime treatment. Instead of (polluted) gypsum, elemental sulfur is produced (only 20 % of the sludge volume vs. gypsum) with the possibility of recycling the sulfur to a sulfuric acid plant.

**SO\textsubscript{2} removal**

The same technological principles can be used to convert SO\textsubscript{2} into H\textsubscript{2}S and/or elemental sulfur. In essence this process uses a buffered sodium carbonate solution as scrubber liquid that absorbs the SO\textsubscript{2} as sulfite. The carbonate buffer is regenerated in an
anaerobic bioreactor where the sulfite/sulfate is reduced to sulfide using e.g. hydrogen or ethanol as reductant. The sulfide can be stripped as hydrogen sulfide or it can be oxidized with air to elemental sulfur. Both options remove the acidity from the system that was introduced through SO₂ dissolution:

\[
\text{SO}_2 + 3\text{H}_2 + \left(\frac{1}{2}\text{O}_2\right) \rightarrow S^0 \quad \text{or} \quad \text{H}_2\text{S} + \text{H}_2\text{O} \quad (6)
\]

The main reaction taking place in the scrubber is:

\[
\text{SO}_2 (l) + \text{H}_2\text{O} \leftrightarrow \text{HSO}_3^- + \text{H}^+ \quad (7)
\]

The carbonate buffer will ensure that the pH remains at the desired value to continue SO₂-absorbtion.

The hydrogen sulfide can be stripped, which will remove the acidity that was introduced through the dissolution of SO₂. The remainder of the sulfide will be removed as elemental sulfur (equation 4), which produces a hydroxyl ion to neutralize the acidity introduced by SO₂ dissolution.

The process is acid-neutral in theory, however, loss of sodium through a small process bleed and caustic consumption due to other compounds in the gas flow (like chlorine, fluoride, etc) still make the addition of a small amount of NaOH necessary. An example of a possible flow scheme is represented below:

![Diagram](image)

Figure 2: Block Process Diagram Biological SO₂-removal

The elemental sulfur produced is re-directed to the anaerobic reactor, where it is converted to H₂S. Although in the above scheme there is always a small percentage of the SO₂ converted to elemental sulfur, the plant design allows for full conversion of SO₂ to elemental sulfur. This introduces a great measure of flexibility to the process. If more H₂S is required than what can be produced stoichiometrically from the SO₂-load, elemental sulfur can be added to the reduction reactor. This way, a very flexible plant can be designed that is capable of producing for example 0 to 25 tons of H₂S per day.
General
Integrating biotechnology in metallurgical flow schemes often requires tailor made solutions. For numerous applications Paques has developed specific flow sheets to best fit the industries needs. In the cases described in this paper examples of these tailor made solutions are provided. Many more process configurations than those described in this paper are possible.

Case 1: Budel Zink, Netherlands

Budel Zink B.V., a Pasminco Ltd. owned company, has operated a zinc refinery at Budel-Dorplein in the Netherlands since 1973. Over 200,000 tons of zinc are produced annually. The conventional roast-leach-electrowin process produces various wastewater streams containing sulfate and zinc. Until mid 2000 these streams were treated conventionally by neutralisation with lime resulting in the production of gypsum.

Increasing legislative restrictions prohibited further production of residues at the Budel Zink site as from July 2000. For this reason alternative wastewater treatment processes were studied over several years in order to come to a process in which production of gypsum is avoided and in which an effluent can be produced which is compliant to the applicable legislation. Paques’ THIOPAQ® technology was selected. This high rate technology converts zinc and sulfate into a zinc sulfide product, which is recycled to the refinery [8].

Figure 3: Overview Drawing of the Full Scale Plant
**ZnSO₄ reduction**

At Budel Zink two streams are treated with this bioconversion process:

- Wash Tower Acid (scrubber discharge from the roaster acid plant). Typically this is about 25 m³/h containing 10 g/l H₂SO₄, 0.5 g/l HF, 1 g/l HCl and 0.5 g/l Zn.
- Magnesium bleed. This bleed is necessary to prevent accumulation of magnesium in the electrolyte. Typically 0.5 m³/h of Purified Solution and/or Spent Electrolyte has to be bled from the circuit in order to control the magnesium concentration. The magnesium bleed contains 15 g/l Mg and up to 300 g/l of sulfate.

The THIOPAQ® plant was realised at Budel Zink in 1999 and forms the heart of the process configuration for high strength sulfate water treatment. The block scheme of the process is presented below:

![Figure 4: Schematic Flow Diagram for the Biological Process Route](image)

1. Neutralisation of Wash Tower Acid with calcine (ZnO).
2. Fluoride removal by precipitation as CaF₂ in a Crystalactor®.
3. Mixing with magnesium bleed (Zn electrolyte).
4. Biological conversion of ZnSO₄ to ZnS, using hydrogen as an electron donor. Hydrogen is produced on-site using a reformer unit, which converts natural gas and steam into H₂ and CO₂.
5. Precipitation and separation of the produced ZnS.
6. De-watering of the produced ZnS.
7. Treatment of the bioreactor effluent in the existing Paques’ groundwater treatment installation where the excess sulfide is converted into elemental sulfur.

**Environmental Impact**

Treatment of the wash tower acid with the conventional neutralisation process led to the production of large volumes of gypsum (18 tons/day) and effluent characteristics which were not compliant to legislation. With the successful implementation of the
THIOPAQ® technology using a high rate sulfate reduction bioreactor no gypsum is produced and an improvement of the water quality has been realised. In addition re-usable calcium fluoride and valuable zinc sulfide are produced. Zinc sulfide (10 t/d) is recycled to the roaster feed.

In the below tables the main data of the Budel plant are summarised:

<table>
<thead>
<tr>
<th>Design capacity</th>
<th>H$_2$S Influent</th>
<th>3200 kg/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production</td>
<td>ZnS</td>
<td>10 t/day</td>
</tr>
<tr>
<td></td>
<td>CaF$_2$</td>
<td>0 – 0.9 t/day</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Water quality</th>
<th>Compound (ppm)</th>
<th>In</th>
<th>out</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SO$_4$</td>
<td>15000</td>
<td>&lt; 300</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>10000</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>500</td>
<td>&lt; 50</td>
</tr>
</tbody>
</table>

**Case 2: Kovohute Pribram, Czech Republic**

The first treatment plant mainly based on sulfur reduction was designed for Kovohute Pribram a.s., located in the heart of the Czech Republic. Kovohute Pribram uses a Varta process [6] to process lead wastes and scrap vehicle accumulators, manufacturing lead and lead alloys. Main end-products are refined lead and silver anodes and pressed, casted and rolled products made of lead or lead alloys.

Kovohute has a recognised ISO 14001-compliant environmental management programme and was awarded the international ‘Health and Safe Environment’ prize by the Prince of Wales Business Leaders Forum in 1998. One of their projects is to treat a slag dump leachate, which is essentially an alkaline carbonate buffered sodium sulfate effluent, containing lead, zinc, tin, and high concentrations of arsenic and antimony. For most of these metals, the effluent discharge standards set by the government cannot be met when using lime treatment. Further, sulfate removal is not required for this application, hence the formation of large quantities of polluted gypsum is undesirable.

Therefore, THIOPAQ® biogenic H$_2$S production technology was selected for the removal of metals from this stream:
A two-stage system was designed. Waste battery acid is used to acidify the strongly alkaline effluent. In the first precipitation stage, arsenic and antimony precipitate as sulphides at a pH of around 3; in the second stage, the remaining metals precipitate out of solution at approximately pH 7. This technology significantly out-performs lime treatment due to the lower solubility of metal sulfides as opposed to hydroxides. Furthermore, the neutralisation of waste acid can be regarded as a bonus of this process configuration.

The plant design offers a great deal of flexibility for Kovohute. The sulfide production rate can be varied from 10 to 75 kg H$_2$S/d (considering that the technology can be designed for over 20 tpd of H$_2$S, this application is a relatively small one). The sulfide can either be produced from elemental sulfur or from waste battery acid.

The equipment, bioreactor and contactors are mounted on a skid at the Paques workshop in the Netherlands. This set-up allows for minimal installation time on site. Considering the corrosive nature of H$_2$S, most hardware is fabricated from plastic.

The plant was commissioned in 2000. Commissioning was quick and successful.

**Case 3 : Caribou Mine, Canada**

The Canadian Company BioteQ Environmental Technologies Inc is currently constructing a sulfur reduction plant at the Caribou Mine of Breakwater Resources Ltd in New Brunswick, Canada. BioteQ has developed the patented BioSulphide Process™ for metal recovery and sulphate reduction, primarily targeting the treatment of effluents produced by the mining industry [10], and which has a similarity to the Paques sulphate reduction technologies. Under the terms of a commercial technology agreement, Paques have supplied the design and engineering for the THIOPAQ® biogenic H$_2$S production technology for Caribou to BioteQ, who are designing and constructing the overall Caribou plant.
Caribou is a zinc mine, which is currently not operating due to low metal prices. The mine, however, continues to operate a lime treatment plant to treat acid mine drainage (AMD) which has an annual average flow of 700 m$^3$/day. The mine also has a sizeable deposit of old tailings containing significant quantities of pyrite, zinc and copper. Over the years these tailings have become a source of acidity and soluble metals due to oxidation and a solution is required to retreat the tailings. BioteQ have contracted with Breakwater Resources to construct a Stage 1 treatment plant to remove metals from the AMD upstream of the lime plant. This plant is scheduled for start-up in October 2001. When the Stage 1 plant is operating successfully, the plan will be to construct a larger Stage 2 plant to allow for the re-treatment of the contaminated tailings concurrently with the ongoing treatment of the AMD.

The Stage 1 plant, shown schematically in Figure 6, will have a planned capacity to treat all of the existing acidic drainage at Caribou. The process plant will recover a saleable zinc/copper concentrate and remove cadmium and lead from the wastewater prior to it entering the existing lime treatment plant for iron and aluminum removal. The treated water will be discharged to local receiving waters within the guidelines of existing permits.

![Figure 6 – Schematic of Stage 1 Treatment Plant at Caribou](image)

In addition to revenues from saleable concentrate products, the plant will reduce lime consumption in the lime plant by an estimated 51% and reduce the volume of sludge produced by an estimated 53%, as well as substantially decreasing the metal content of the lime sludge product. The savings in lime consumption and the reduction in sludge disposal costs, together with revenues from concentrate sales will offset operating costs of the lime plant and, depending on metal prices, may make a small operating profit.

On reaching predetermined performance criteria, BioteQ and Breakwater will expand the first stage plant to allow the re-treatment of contaminated tailings, which are currently stored at a site separate from the main tailings impoundment. The contaminated tailings contain significant levels of mobile metals that will be leached in a controlled manner utilizing existing acid drainage and then recovered in a THIOPAQ$^\text{®}$ / BioSulphide$^\text{tm}$ plant. The treated tailings could then be deposited in the existing tailings impoundment.
The Stage 2 plant, shown schematically in Figure 7, will have a designed capacity of 2100 m$^3$/day and will allow the processing of 210 tonnes/day of contaminated tailings. In addition to treating the ongoing acid drainage at Caribou as described above, the Stage 2 plant will selectively recover copper and zinc from the leached tailings and reduce cadmium and lead levels in the treated tailings. Approximately 1 million pounds of copper and 4.2 million pounds of zinc will be recovered annually.

![Figure 7 - Schematic of Stage 2 Treatment Plant at Caribou](image)

**Conclusions**

High rate, engineered bioreactor systems offer many possibilities for application in mining and metallurgy. The reduction of sulfur compounds with the subsequent production of either reusable sulfur or H$_2$S has been proven on industrial scale and is a mature technology.

Safe and robust biological processes can serve to recover metals and remove sulfur compounds. In some cases, the recovery of metals as saleable products can result in profitable water treatment.

Current and potential applications include:

- Low cost H$_2$S production for use as a reagent in metallurgical processes
- Selective metal recovery from metallurgical and waste streams
- Metal reduction for environmental control
- Sulfate reduction and removal to meet environmental regulations
- Sulfate reduction to allow recycle of industrial water
- SO$_2$ removal by conversion to H$_2$S and/or elemental sulfur
References


