High rate biotechnology for the metal and mining industry

By Martijn Olde Weghuis

Budel zinc refinery - hydrogen gas lift loop reactor for sulphate reduction and zinc recovery.

Two step Sulfateq plant at FMI.

More than 30 years ago, the Dutch company Paques pioneered the commercial development and application of anaerobic technology for wastewater treatment in the Netherlands. It started with the application of Upflow Anaerobic Sludge Blanket reactors for the production of biogas from wastewater.

Paques' first anaerobic installation in Canada was commissioned in 1988 for a client in the pulp and paper industry. Tembac's Temiscaming pulp mill selected BIOPAQ IC (Internal Circulation) technology to treat 600 m^3/h of effluent, which contained 120 tpd of COD. The plant was commissioned in January 2006. Biogas produced replaces natural gas as fuel to the pulp dryers and is desulphurized with THIOPAQ technology to H_2S concentrations below 10 ppmv.

THIOPAQ technology was originally developed for the biological desulphurization of biogas produced in anaerobic reactors for heat or power generation. The first full scale installation was in 1990 in the Netherlands. Nowadays, the technology is applied for the removal of several kilograms to several tons of sulphur per day. It is also used for the desulphurization of natural gas, or other gases, from the petrochemical industry or gasification processes.

For applications in the oil and gas market, the technology is marketed by Paqell (a joint venture with Shell Global Solutions) under the name THIOPAQ O&G.

The technology relies on the physical-chemical absorption of H_2S into a mild caustic solution and the almost complete regeneration of the caustic by bacteria in a separate bioreactor. Elemental sulphur produced (biosulphur) is an excellent product for fertilizer applications, or use as a fungicide. It is hydrophilic and has a particle size between 10-40 µm. Experiments in the field with Breton Canola showed a 30 per cent higher grain yield for biosulphur, compared with the application of Claus sulphur. Paques has developed a fertiliser product, based on the unique properties of biosulphur.

Sulphate removal and metal recovery

Complete control of the biological sulphur cycle and a track record in anaerobic and aerobic technology can be applied in the metal and mining industry. Typical applications are removal of sulphates, and recovery of metals from mining or metallurgical effluents. Selecting the right population of microorganisms for bioreactors designed to handle large flows, while retaining high concentrations of the desired microorganisms, is crucial for success in this heavy-duty industrial environment.

Two examples of sulphate reduction and metal recovery are plants designed, built and commissioned by Paques in 1992 and 2000 for a zinc refinery in the Netherlands. The first plant was designed for treatment of sulphate (7.2 tpd) and recovery of zinc (0.7 tpd) as zinc sulphide from low sulphate containing waters (300 m^3/hr). In this installation, ethanol is used as electron donor for the reduction of sulphate to sulphide.

Six years later, a plant was commissioned on the same site to treat a high sulphate combined stream containing the bleed from the gas cleaning section of the acid plant and an electrolyte bleed. This combined stream (ca. 25 m^3/hr) is high in sulphate (15 g/l) and zinc (10 g/l). In this plant, hydrogen which is produced from natural gas in a steam reformer unit is used as electron donor.

For both installations, excess sulphide that is left after precipitating zinc and other metals is treated in sulphide oxidizing bioreactors. Sulphate concentration in the effluent was around 250 mg/l, sufficiently low for discharge.

In conventional treatment of similar effluents, lime milk is used to produce high volumes of gypsum. With high rate biotechnology, less solid waste is produced and metal sulphides and sulphur produced can be recycled to the roaster. Implementation of biotechnology made this zinc refinery the first gypsum free refinery in the world.

Technology for sulphate reduction combined with metal recovery and/or sulphide oxidation is marketed under the name SULFATEQ.

Sulphate reduction technology for acid mine

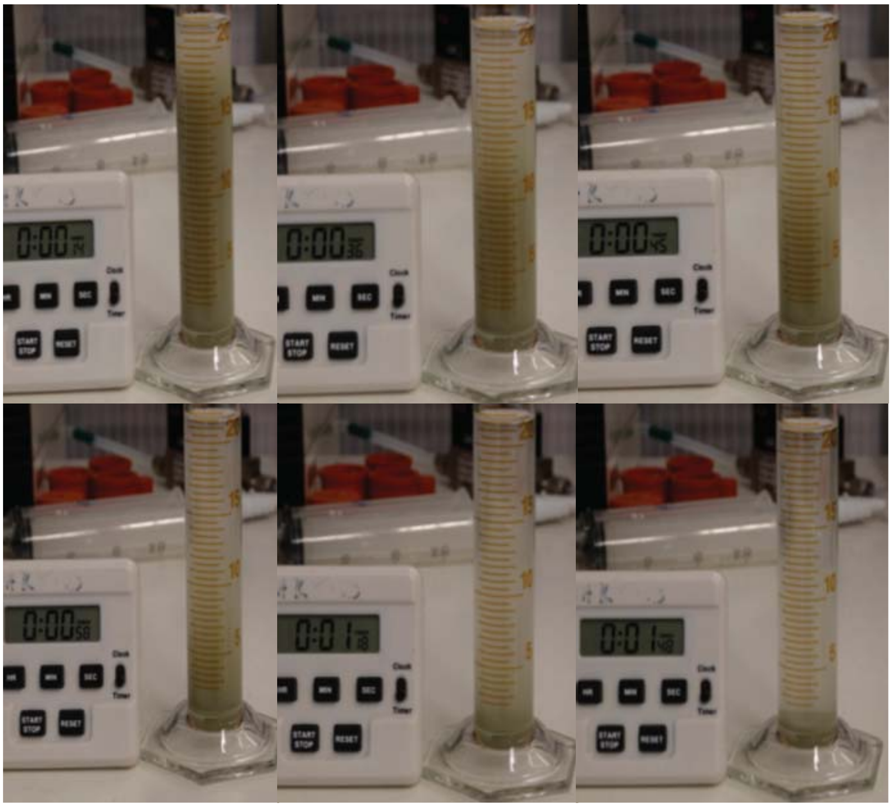
In 2003, Paques successfully commissioned a demonstration plant for the treatment of 125m^3/hr of gypsiferous acid mine drainage, to reduce sulphate from 2.4 g/l to less than 300 mg/l and increase pH from 2.9 to 8.5. The aim was to reduce the scaling tendency of the water used in the coal washing process.

At the Sierrita mine site in Arizona, Freeport-McMoRan Copper & Gold Inc. is currently demonstrating different new water treatment and resource recovery technologies at 100 gallon per minute scale. Based on Paques' SULFATEQ technology, the plant was designed and commissioned in August 2012. In this plant, sulphate is biologically converted to solid elemental sulphur in a two step process.

In the first bioreactor, sulphate is reduced to hydrogen sulphide using hydrogen gas as electron donor. In the second bioreactor, hydrogen sulphide is oxidized to elemental sulphur using air. Besides sulphate removal, a significant reduction in total salinity is achieved, as a large part of the dissolved calcium is precipitated as calcium carbonate.

The intermediary hydrogen sulphide compound can also be used to selectively recover metals like copper and zinc from process water and wastewater streams. Efficient chemical precipitation results in valuable metal sulphide concentrates, that can be processed by smelters to produce different high quality metals.

Effluent concentration is well below the projected level of < 250 mg/l sulphate. The solids produced in SULFATEQ plants are dewatered using a filter press.



Settling tests of bioscorodite crystals harvested from semi-pilot Thioteq-scorodite bioreactor.

Economic metal recovery

Metal sulphide precipitation is well accepted for the recovery and removal of intermediate concentrations of metals like copper, arsenic, zinc, nickel, cobalt and zinc from water. The sulphide is mostly obtained from chemical sources such as Na_2S, NaHS or H_2S. Costs to receive on-site and handle and store these sulphide compounds safely can be high.

Paques has developed a cost-effective and efficient alternative to the traditional sources of sulphide: THIOTEQ-Metals. In this process, H_2S is produced on-site by bacteria that reduce a concentrated sulphur-containing feed. The technology is based on a bioreactor, where elemental sulphur is converted into hydrogen sulphide for the selective precipitation of metals. As with sulphate reduction, bacteria consume a reductant like ethanol or hydrogen, or other organic compounds. Costs for the reductant are four times less with elemental sulphur as sulphur source. Typically, bacteria are not in contact with the metal-containing water, but "offline".

An installation based on Paques' THIOTEQ technology has been commissioned at a goldmine in the Americas. Here, tons of copper are recovered as copper sulphide from effluent, which would

Paques IC reactors (left) and CIRCOX reactors (right).

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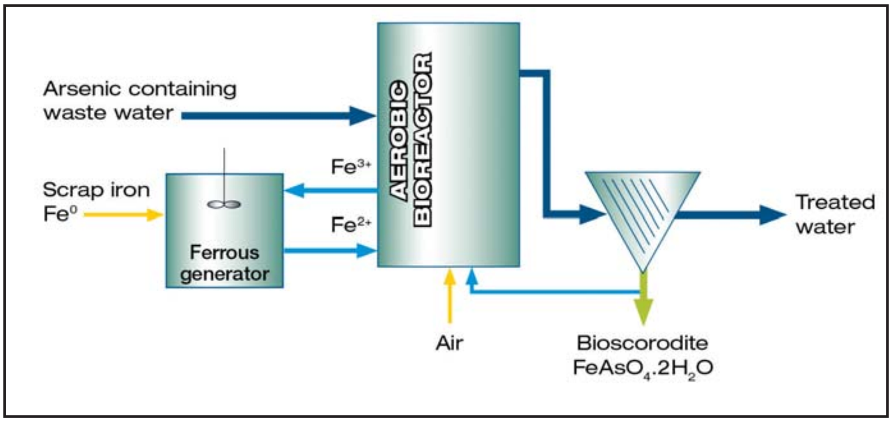
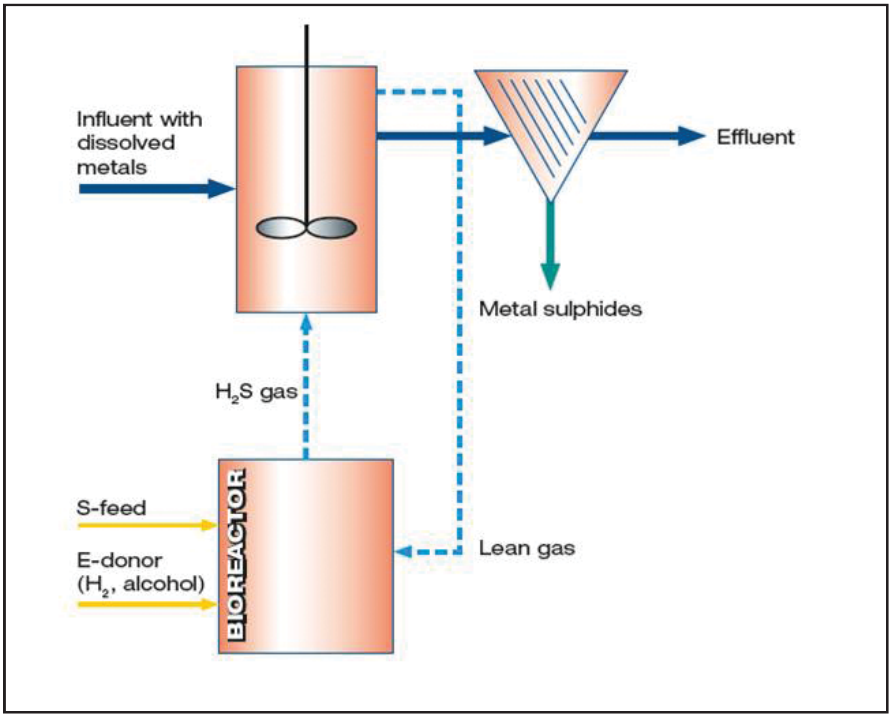
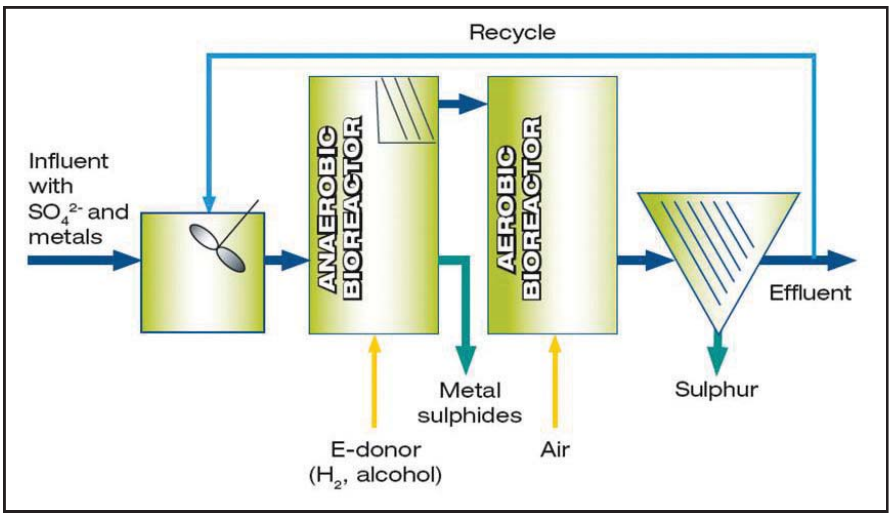


The simplified process for immobilization of arsenic as bioscorodite.



Thioteq process for H_2S generation - bioreactor contactor and metalsulphide settler.



Two step Sulfateq process for sulphate removal and metalsulphide recovery

otherwise have been lime treated to produce copper-contaminated gypsum.

Arsenic immobilization

Currently, Paques is further developing a patented process (THIOTEQ-Scorodite) for arsenic immobilization, based on work by Wageningen University's Dr. Paula González Contreras. Arsenic is a toxic element that cannot be reused and large amounts have been collected from metallurgical processes as arsenic trioxide. There is no market for the tons of arsenic released from metallurgical processes. A time-stable discard product is essential. Only scorodite, which occurs naturally as a stable mineral in nature, fits that requirement.

Combining bio-crystallization and aerobic air-lift loop reactor technology has several advantages compared to traditional precipitation tank reactors.

The aerobic process is a new sustainable solution to arsenic removal and its immobilization. In this process, a compact air-lift loop reactor (CIRCOX–technology) is the basis for the production of arsenic-containing crystals, i.e., bioscorodite crystals. Biogenic scorodite production in CIRCOX reactors is the result of a successful balance between bio-oxidation and crystallization reactions. Since 1987, Paques B.V. has gained extensive full-scale experience with more than 30 CIRCOX bioreactors, treating diverse wastewaters. It is expected that the process can be implemented at full-scale in a relatively simple manner.

Combining bio-crystallization and aerobic air-lift loop reactor technology has several advantages compared to traditional precipitation tank reactors. Bioscorodite crystals are suspended in an aeration-induced circular liquid flow. This minimizes scaling and mechanical problems. Crystal retention in the reac-

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tor is improved by the high density of bioscorodite and large crystals, which are also older crystals and therefore more stable than nascent ones. Harvested crystals are selected by their sedimentation rates, assuring high stability values.

Microorganisms play a key role in the production of bioscorodite, precipitating arsenic at 70°C, instead of the higher temperatures and pressures used in autoclaving technology. These extreme microorganisms grow by oxidizing iron, in the presence of arsenic, as free cells in suspension and at low pH values.

Operational costs are reduced when compared with chemical precipitation. This is mainly due to the fact that no chemical oxidant is needed. Air is used as the oxidant. Furthermore, formation of gypsum is reduced to a minimum because no seeding material is needed and less neutralization with lime is required. The result is a pure, stable and compact crystalline product. Harvested bioscorodite crystals are large in size, have a high arsenic content (30 wt%), low free water content (<3% free water on settled samples), and they have exceptional stability properties based on arsenic leaching values in TCLP tests. These properties enable disposal of the crystals immediately after being harvested.

Scorodite mineral and bioscorodite crystals.

An immediate application of this process is treatment of streams where arsenate is present, such as effluents from (bio) leaching operations.

Arsenic stabilization is going to be one of the most important environmental issues facing metallurgical companies when disposal legislation becomes stricter. Converting arsenic into bioscorodite can lower environmental risk and provide important cost savings to the company.

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