

Focus on CSIR Research in Pollution and Waste

Technologies for waste and wastewater treatment

Background

The Pollution and Waste Group of the CSIR specialises in the development of practicable treatment solutions for waste and wastewater arising from numerous industrial sectors.

The group's objective is to resolve potential pollution problems at mines and industries by applying suitable technologies, which are in many instances engineered for the site-specific and often unique nature of the waste or wastewater.

The challenge

High concentrations of sulphate are associated with certain industrial waste streams. In addition, elevated sulphate concentrations are often present in ground and surface water associated with mining due to bacterial and chemical oxidation of pyrite (FeS) resulting in acid mine drainage (AMD). AMD has the potential to cause serious environmental pollution.

Sulphate removal technologies

With support from the Technology and Human Resources for Industry Programme (THRIP), which aims to boost South African industry by supporting research and technology development, and by enhancing the quality and quantity of appropriately skilled people, the CSIR has developed three world class technologies to reduce or remove sulphate from waste streams.

These include:

- The limestone neutralisation technology
- The barium sulphide process
- The biological sulphate reduction/removal technology.

Limestone neutralisation

The CSIR's patented limestone/lime treatment process has been implemented on several industrial plants and is now globally

recognised by leading engineering firms as the best practice for water treatment in various applications.

Through this approach:

- Acid is neutralised with the cheapest alkali. Acid removal is achieved within 20 minutes in a fluidised-bed reactor where crushed limestone with a particle-size less than 4 mm is used
- Sulphate is removed from concentrations as high as 20 g/l (as SO_4) to less than 2 g/l, the solubility of gypsum
- Metals are precipitated as metal hydroxides. If the acid water is rich in iron (II), it is oxidised prior to the neutralisation stage. Iron (II)-concentrations of 3 g/l (as Fe) are completely oxidised within two hours reaction time.

Besides cost savings, the benefits of this process are that:

- The pH is controlled naturally at neutral or near-neutral values
- A small reactor with contact time of only 15 minutes is needed
- High-density sludge is produced
- By-product recovery is possible (e.g. CO_2 -gas and gypsum)
- The limestone is safe to handle
- Water with a propensity to form gypsum scale is stabilised.

The GypSLiM process – waste gypsum to sulphur/sulphuric acid, limestone and magnesite

The removal of sulphate pollutant from water has traditionally resulted in the build up of large amounts of wastes, primarily gypsum (calcium sulphate). The CSIR has demonstrated a technology using waste gypsum to profitably produce valuable sulphur and/or sulphuric acid, limestone and magnesium carbonate. The products (sulphur & magnesium carbonate) are normally imported in vast quantities through South African ports, whereas the GypSLiM



process can turn waste and environmental liability into profit at various inland/coastal sites.

Sulphate precipitation process

This process is based on the insolubility of barium sulphate, and consists of two parts:



- Water treatment, where barium sulphide, oxide or carbonate is dosed to sulphate containing water, which results in a barium sulphate precipitate
- Thermal reduction, where the barium sulphate sludge from water treatment is reduced at 1200 °C to BaS or BaO.

This technology, based on simple chemical precipitation, can remove sulphate to low levels. The capital cost of treatment plants are low, requiring only 15 minutes residence time and basic turbidimetric dosage control.

Biological sulphate removal

The CSIR developed the biological sulphate removal technology in 1984. A pilot plant single stage reactor was developed in 1998, resulting in partial removal of the formed sulphides. Sulphate can be removed biologically needing cost-effective carbon and energy sources, while the biological sulphide removal is dependent on a small supply of air.

Waste streams containing concentrations as high as 3 g/l sulphates have been treated and concentrations as low as 0.2 g/l sulphate have been obtained within four to six hours' reaction time applying the biological treatment.

Contact details:

CSIR Natural Resources and the Environment

Linda Godfrey
Manager: Pollution and Waste

Tel: +27 12 841-3675
Fax: +27 12 842-7687
Email: lgodfrey@csir.co.za

www.csir.co.za

The benefits of this development include:

- Lower capital costs, as fewer stages are involved and lower retention times are obtained
- Lower running costs, due to better utilisation of the carbon source
- The process is more stable because of the lower sulphide concentrations.

Fluoride removal

Several industries produce wastewater with elevated fluoride concentrations. Natural waters can also contain elevated fluoride concentrations depending on the levels of fluoride that occur naturally in the soils. The CSIR has developed a water treatment method that can remove fluoride and make the treated water safe for re-use or release into the environment and for human consumption.

Full-scale applications

Research conducted by the CSIR has made a significant contribution to the treatment of waste and wastewater rich in acid and sulphates. The CSIR, together with leading licensed engineering companies assisting as implementation partners, have been able to construct reference and full-scale plants both in South Africa and internationally, e.g. Australia.

The following developments have been implemented on full-scale:

- The robust, limestone handling and dosing system, which was developed using waste CaCO₃ from the paper industry
- A limestone neutralisation process in which a fluidised-bed reactor was used for the neutralisation of acid water, rich in metals, using crushed limestone
- In the integrated iron (II)-oxidation/limestone neutralisation process, powdered limestone was used as catalyst for the iron (II)-oxidation for the neutralisation and gypsum crystallisation processes, occurring in the same reactor. The novelty of this development lay in the finding that iron (II) can be oxidised at pH 6, which was achieved using limestone. Previously lime was used to raise the pH to 7.2 at which pH the iron (II)-oxidation rate was rapid
- The partial sulphate removal applying the gypsum crystallisation technology comprises a process that utilised limestone and lime for removal of sulphate to below the saturation level of gypsum. In the first stage, acid water is neutralised with limestone while CO₂-gas is released. This is followed by lime treatment to pH 12 in the next stage, achieving maximum

gypsum crystallisation. After sludge separation, the water is treated in a third stage where the high pH water from the second stage is contacted with the CO₂-gas produced in the first stage. This results in pH adjustment to 8.6 and precipitation of CaCO₃, a valuable by-product, which can be recycled to the first stage

- With the biological sulphate removal process, sulphate is removed by using organic material (e.g. ethanol, sugar, mixture of H₂ and CO₂ gas (80%:20%) or fermentation products of grass-cellulose) as the carbon and energy source.
- Findings emanating from the above CSIR research have been published in international scientific journals, presented at international conferences, supported two PhD and eight MSc degrees and received seven national and international science awards for major contributions in industrial water technology. Several patents registered in South Africa, the USA and other strategic countries protect the core technologies and intellectual property of the organisation.

Relevance to South Africa and the rest of the world

The technologies mentioned above have a direct impact on the improvement and protection of the environment, whilst supporting South African industry in its day-to-day operations. Through the implementation of cost-effective treatment technologies, good quality water can be discharged back into the environment.

The construction cost of the neutralisation plants that have been constructed or are under construction between 2000 and 2007 amounts to more than R90 million. Full-scale implementation of these technologies have contributed to job creation, as well as significant cost savings to companies that have switched to these technologies. Opportunities for product recovery, e.g. sulphur production/regeneration on an industrial scale, have been identified in a drive towards industrial ecology and waste symbiosis.

The development work undertaken by the CSIR to date, will be optimised and applied in new, innovative applications, e.g. treatment of SO₂-rich gases, responsible for atmospheric pollution, thereby supporting the vision of national government in reducing, reusing and recycling waste.