## Technologies for sulphate removal with valorisation options

Mona Arnold<sup>1</sup>, Mariekie Gericke<sup>2</sup>, Ritva Muhlbauer<sup>3</sup>

<sup>1</sup>VTT, Technological Research Centre of Finland ltd, Finland, mona.arnold@vtt.fi <sup>2</sup>Mintek, South Africa, mariekieg@mintek.co.za <sup>3</sup>Anglo Coal, South Africa, ritva.muhlbauer@angloamerican.com

## **Extended Abstract**

One of the major challenges confronting the mining and minerals processing industry in the 21st century is the management of water in an environment of ever decreasing water resources. Especially polluted mine water, from both active and abandoned mines represent a major problem worldwide. Discharge from the latter has been recognised as the main cause of 7% of failures to achieve the goals of the Water Framework Directive (2000/60/EC).

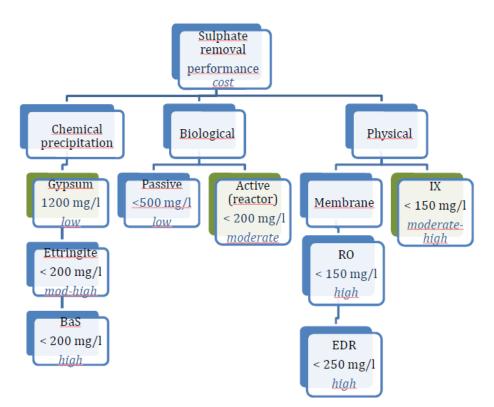
The treatment of mine water has generally focused on the removal of (heavy) metals. Less attention has focused on mitigation of dissolved sulphate levels due to its lower environmental risks and regulatory standards when compared to those for acidity and dissolved metals. However, regulatory agencies are becoming increasingly concerned over elevated SO4-concentrations in effluents with discharge limits sometimes as low as 10mg/L, but typically between 250 mg/L and 1,000 mg/l. The rationale for imposing sulphate discharge limits range from more generally accepted aspects of salinity contributions from high concentrations of sulphate, to more controversial aspects such as the putative effects of sulphate on mercury methylation by sulphate-reducing bacteria, or purported chronic aquatic toxicity.

Figure 1 gives an overview of the current commercially available technologies for sulphate removal. Mine location, climate, water characteristics, available utilities, footprint, and disposal areas all preclude a "one-size fits all" solution. Currently the most widely used method for mine water treatment is lime precipitation in which acidity is neutralized and metals precipitated as hydroxides by adding lime or limestone. Although this process successfully removes the metals and increases the pH to neutral levels, the resulting effluents contain high levels of sulphate (1 500 - 2 000 mg/l), well above the permittable discharge levels (Table 1).

Sulphate limits range from 2000 mg/L for surface water discharge in Finland and Chile to 10 mg/L in the US state of Minnesota (International Mining 2013; Minnesota Pollution Control Agency 2014). In British Columbia/Canada a 30-day average sulphate concentration guideline of 65 mg/L has been proposed, and other provinces are also considering lower limits for sulphate.

<b>Table 1</b> Sulphale discharge levels.		
Authority	Sulphate Concentration (mg/L)	
USA	10-500	
Canada	500	
Finland	2,000	
South Africa	200-600 (evaluated on a case-by-case basis)	
Australia	1,000	
World Health Organization (drinking water)	250	

Table 1 Sui	lphate discl	harge levels.
-------------	--------------	---------------



*Figure 1* Sulphate removal technologies, average removal efficiency and costs. Based on e.g. Mattson (2014) and Mierzejewski (2014). Technologies in green indicate possibility for solids productification or valorisation

Further reduction in the sulphate levels is well below the capability of lime precipitation. However, achieving low solute concentrations to comply with discharge limits in an economically viable process is challenging and additionally requires sustainable and economically viable solids waste management. Biochemical methods have mainly been used as an inexpensive passive treatment system for removal of metals and sulphate by reducing sulphate to hydrogen sulphide using sulphate-reducing bacteria with concomitant precipitation of metals within the pit or passive reactor. However, compared to active processes performed in controlled reactors, metal removal from passive systems is difficult and does currently not result in recovery of metal values.

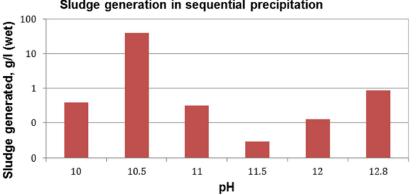
All treatment technologies produces a residual or by-product which will require additional treatment. It is thus somewhat surpising that the valorisation aspect of sulphate laden mine water treatment seems to only be in the beginning phases of development and little work has been published in this field. Examples of successful recovery of Cu and Zn from process streams are described using the Paques ThIOTEQ<sup>TM</sup> and SULFATEQ<sup>TM</sup> technologies. Elemental sulphur can also be recovered from biological sulphate reduction processes and could be potentially re-used for sulphuric acid production.

Tests have been conducted at Mintek in multi-stage columns (Figure 2) at ambient around 20°C using cellulose-based substrates. The pH levels of the water could be successfully increased to levels >6. Reducing conditions could be maintained and removal of sulphates (80-90%) and base metals were demonstrated. The work will continue developing the with recovery of elemental sulphur from the reactors.



Figure 2 Multi-stage column system used for test work

Figure 3 gives the results of sequential precipitation of the water from a Finnish Gold mine. It gives a clear indication of the optimal pH for precipitation (10.5) and further analysis of the generated sludge (10.5). Detailed chemical analysis of the generated solids will form the base for developing the valorisation concepts. The generated solids contain little base metals but the minerals of potential industrial value are magnesium and manganese.



Sludge generation in sequential precipitation

Figure 3 Sludge generated in sequential precipitation

Although there are a number of technologies available for producing an effluent that can be reused or safely released into the environment, the focus should in future be on the development of concepts that can enable valorisation of the components of the effluent or solid waste generated, focusing on recovery of beneficial metals and development of less energy consuming processes.

Key words: IMWA 2016, full paper, writing, tables, figures, reference

## References

Mattson, B. (2014) Review of Sulfate Treatment Issues: an update of INAP Treatment of Sulfate in Mine Effluents Presentation at INAP Sulfate Treatment Workshop Feb 27-28, 2014- Salt Lake City

Mierzejewski, M. (2014) The Challenges of Removing Sulfate from Mining Wastewaters. INAP Sulfate TreatmentWorkshop Feb 27-28, 2014- Salt Lake City