The biological Sulphate removal technology

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ABSTRACT

Mining is implicated as a significant contributor to water pollution, the prime reason being, that pyrites oxidize to sulphuric acid when exposed to air and water. Mine effluents, often containing sulphate, acidity and metals, should be treated to render it suitable for re-use in the mining industry, for irrigation of crops or for discharge in water bodies. This study describes the removal of all three mentioned pollutants in mine effluents, from different origins, containing different concentrations of various metals. The objectives were achieved, applying the biological sulphate removal technology, using ethanol as the carbon and energy source. It was shown that diluting the mine effluent with the effluent from the biological treatment, the pH increased due to the alkalinity in the treated water while the metals precipitated with the produced sulphide. When this treatment regime was changed and the mine water was fed undiluted, it was found that the metals stimulated the methanogenic bacteria (MB) as trace elements. This resulted in a high COD utilization of the MB, such that too little COD was available for the SRB. Metal removal in all three studies was observed and in most instances the metals were eliminated to the required disposal concentration.

INTRODUCTION

The scarcity of water, due to low rainfall, in South Africa is exacerbated by pollution of the surface- and groundwater resources due to industrial activities such as mining of minerals. By its very nature and scale, mining makes a marked and visual impact on the environment. Mining is implicated as a significant contributor to water pollution, the prime reason being, that most of the geological formations which are mined contain pyrites which oxidize to form sulphuric acid when exposed to air and water.

The combination of auto-oxidation and microbial sulphur and iron oxidation produces large volumes of sulphuric acid, which are highly corrosive and when discharged in the river systems can cause major environmental problems, one of them being the high toxicity level for the aquatic biota. This mining related polluted, often acidic and sulphate rich water is referred to as Acid Mine Drainage (AMD). While a mine is operational, the act of mining (e.g. sinking of shafts or open pits and the excavation of overburden and ore) can have a significant impact on the natural water environment, as mining activities inevitably disrupt pre-existing hydrological pathways (Younger and Wolkersdorfer, 2004). Waste products from both mining and mineral processing operations are often contained in large heaps or in tailings dams. Seepage of contaminated leachate from waste rock piles and tailing dams is a significant cause of surface and ground water pollution in many mining areas. This kind of water pollution often occurs when the mine is in operation and without remediation can persist long after mine closure (Younger and Wolkersdorfer, 2004).

Acid mine water should be treated in order to render it suitable for re-use in the mining industry, for irrigation of crops or for discharge in the rivers and dams. Because of the variety of mine waters encountered in nature and because of the familiarity of the mining sector with the physical and chemical processes, necessary to separate metals and water, there is a wide range of conventional treatment methods for mine waters (Younger *et al.*, 2002). Mine waters can be treated *chemically* applying lime and limestone neutralization technologies (Maree et al, 2003), however the residual sulphate in the form of gypsum ($CaSO_4$) is dependent on the solubility of gypsum, which is measured at about 1500 mg/ℓ as sulphate (SO_4). For removal of sulphate below this concentration, the *biological* sulphate reduction technology can be applied (Greben et al, 2000a, 2000b, Maree et al, 2004a). In order to achieve biological sulphate reduction, anaerobic conditions, favoured by the sulphate reducing bacteria (SRB), and the presence of suitable carbon and energy sources, have to be adhered to.

Successful sulphate reduction is typically associated with a pH increase due to the production of alkalinity. Therefore, the biological sulphate reduction technology is particularly beneficial to mining industries experiencing acid mine drainage problems, as it results in removal of sulphate, in a pH increase of the treated water and often in metal removal. The latter occurs as a result of the production of sulphides, followed by metal precipitation to form metal-sulphides. The SRB utilize organic products as the carbon and energy source, providing electrons, while sulphate is used as the terminal electron acceptor with hydrogen sulphide (H_2S), CO_2, H_2O or HCO_3^- and acetate as the end products (Greben et al., 2002). In this study mine effluents, containing sulphate, acidity and metals, from three different mines are treated biologically, using ethanol as the carbon and energy source.

The objective of this study is to show that metals containing acid mine water should be diluted with the effluent of the biological sulphate removal process, so that the metals are precipitated as metal sulphide and that the acidity of the mine water is neutralised with the alkalinity of the biological treated water *prior* to feeding the mine effluents to the biological sulphate removal reactor.

MATERIAL AND METHODS

In this paper investigations are described using three different mine waters as feed water in each study. The mine water originated from 1) an active coal mine, 2) a copper and nickel mine and 3) from a passive coal mine, all located in Southern Africa. The treatment of the different mine effluents are presented in three separate studies.

Feed water
The chemical composition of the three mine effluents is presented in Table 1. The feed water was supplemented with 1.5 mℓ ethanol/ℓ feed water as the carbon and energy source. This resulted in a COD/SO_4 ratio of ≈ 1 (Rinzema & Lettinga, 1988; Greben et al., 2004).

Reactor configuration: Single - stage completely-mixed reactor
The completely-mixed reactor system used in all three studies comprised of a reactor (volume15 ℓ) and a clarifier (volume15 ℓ, Fig. 1). Both reactor and clarifier were open to the atmosphere so that air could partly diffuse into the reactor system. A sludge recycle was in place from the bottom of the clarifier to the top of the reactor. The return sludge flow rate was maintained at 4x the feed flow rate. The operational temperature was maintained at 20-22 °C.

Biomass
The reactors received to sulphate adapted biomass, obtained from the CSIRosure reactor (Witbank, South Africa), of which the VSS was 11.9 g.

Analytical
Manual determinations of sulphate, sulphide, alkalinity, COD, pH and metals were carried out according to analytical procedures as described in Standard Methods (APHA, 1985). With the exception of the MLSS, VSS, sulphide and feed COD, all analyses were carried out on filtered samples (Whatman #1). The COD samples were pre-treated to eliminate the sulphide contribution to the COD concentration with a few drops of H_2SO_4 and N_2 gas.

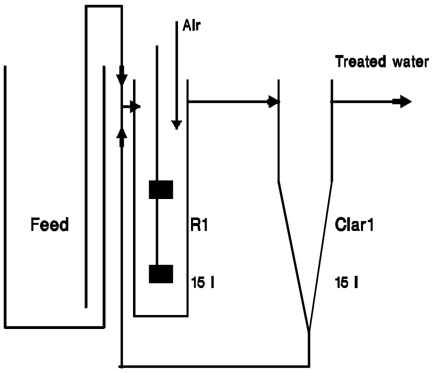

Figure 1: Completely-mixed reactor

Origin Mine Water			
Parameter (Except for pH in mg/ℓ)	**Active Coal Mine**	**Copper and Nickel Mine**	**Closed coal mine**
pH (units)	3.2-3.5	4.3-6.5	3.5
Acidity	600		
Alkalinity		100-130	
Sulphate	2500-3150	1600-2250	2600
Ammonia	0.06		
Calcium	305		
Magnesium	178		103
Iron	139		76
Aluminium	11.7		< 0.07
Manganese	8.4	0.97-0.99	9.3
Copper	0.35	0.01-0.05	0.75
Zinc	113	1.25-38	4
Nickel		5.5-5.86	0.61

Table 1: Chemical composition of the three mine effluents

Experimental

Study 1
During study 1, the influent to the reactor initially comprised artificial feed water. Thereafter, AMD was diluted with the effluent of the biological treatment system, prior to feeding it to the reactor, with the aim to increase the pH as well as to partly precipitate the metals present in the AMD. The experimental periods were determined by the different Hydraulic Retention Times. These conditions are presented in Table 2.

	Synthetic Feed water	AMW: Treated water			AMD	AMD
Dilutions	Undiluted	1:1	1:1	1:1	Undiluted	Undiluted
HRT (h)	12	10	5.3	4.3	18	14.4

Table 2.: The experimental periods determined by AMD dilution and HRT

Study 2

Study 2 was divided in four experimental periods, which were determined by the feed rate and the sulphate concentration in the feed water. The experimental periods are depicted in Table 3. During study 2, AMD was undiluted and not pre-treated with the effluent as feed water to the reactor system.

Period	Days	Feed rate (ℓ/d)	HRT (h)	SO_4 conc. Feed (mg/ℓ)
1	1-12	15	24	1600
2	13-23	30	12	1600
3	24-29	30	12	2100
4	30-46	15	24	2250

Table 3: The experimental periods during study 2

Study 3

The experimental period of study 3 was 34 days. The HRT was 24 h from day 1-20 and 18 h from day 21-34. As during study 1, the AMD, which had an acidity of 1200 mg/ℓ and a pH of 2.5, was diluted with the effluent of the biological reactor in a ratio of 1:1.

RESULTS AND DISCUSSION

Sulphate removal and the sulphate reduction rates

Study 1

The sulphate removal rate results as obtained from Study 1 are presented in Table 4.

	Synthetic Feed water	AMW: Treated water			AMD	AMD
Dilutions	Undiluted	1:1	1:1	1:1	Undiluted	Undiluted
HRT (h)	12	10	5.3	4.3	18	14.4
Rates						
SO_4 red rt g/(ℓ.d)	2.5	2.9	6.2	8.4	2.5	4.9
Ratios						
COD/SO_4^{2-}	0.82	0.63	0.84	0.68	0.8	0.55
S^{2-}/ SO_4^{2-}	0.16	0.17	0.2	0.15	0.09	0.1

Table 4: The sulphate removal results as obtained during study 1

The results show that the sulphate reduction rate was 2.5 g SO_4 (ℓ.d) at a HRT of 12 h, feeding synthetic feed water. When feeding the AMD: effluent mixture (1:1), the reduction rates increased from 2.9 to 8.4 g SO_4 (ℓ.d), when the HRT decreased from 10-4.3 h. The improved sulphate reduction rate can be ascribed to the higher feed rate (lower HRT) as well as to the adaptation time of the sulphate reducing bacteria (SRB). This finding agreed with that of other researchers indicating that sulphate removal efficiency improved with time (Visser, 1995).

The results in Table 4 further indicated that the sulphate removal rates were 2.5 and 4.9 g SO_4 (ℓ.d), when undiluted AMD was fed to the reactor and when the HRT decreased from 18 to 14.4 hours. These results show that the sulphate removal progressed very well, since the reactor pH increased from 3.2 and 3.5 to 8.2 and 7.9, respectively, due to the increased alkalinity production. Sulphide and alkalinity are both products from the biological sulphate removal process. Direct feeding of acid mine water, without pre-neutralisation offers benefits for full-scale implementation as neither lime nor limestone treatment nor a separate stage for pre-neutralization is required.

Study 2

The results as obtained from study 2 are given in Figure 2 showing the sulphate concentration in the feed and treated water, as well as the COD of the treated water over a period of 46 days in the reactor.

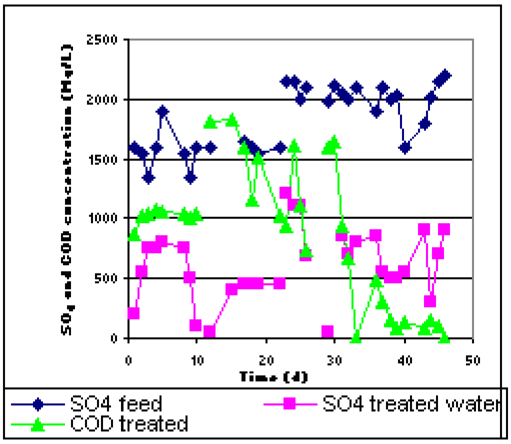

Figure 2: The SO_4 and COD concentration in the feed and treated water

It was observed that sulphate was almost totally removed from the feed water after 10 days to 50 mg/ℓ (as SO_4). The initial HRT was 24 h, which was reduced to 12 h after day 10. Thereafter, the sulphate was reduced to a consistent 450 mg/ℓ in the treated water. In the third batch of feed water the sulphate concentration increased to values of and over 2000 mg/ℓ and the reactor pH was as low as 5.21, resulting in a sulphate concentration in the treated water of 1150 mg/ℓ. Because of this low feed water pH, the reactor pH decreased, which resulted in poor sulphate removal. Visser (1995) showed that the highest sulphate reduction was achieved when the reactor pH was 7.5-8.0. When the reactor pH was increased with a 50 g $NaHCO_3$/ℓ solution and the reactor was operated in a batch mode (days 27-29) at the same time, the sulphate was reduced to 50 mg/ℓ.

Another feed batch was introduced to the reactor on day 30. The HRT was increased to 24h on day 31, with the aim to reduce the sulphate concentration in the effluent to values lower than 200 mg/ℓ. The reactor pH was strictly monitored from day 30 onwards and when it decreased to values lower than pH of 7.5, a small volume of a concentrated $NaHCO_3$ solution was added to the reactor. Although the reactor was closely monitored from day 30 onwards, the sulphate concentration in the reactor did not decrease to values lower than 500 mg/ℓ. When observing the results of the different parameters, it was noted that the reactor COD concentration had decreased dramatically. When on day 43, additional ethanol was added straight to the reactor, the SO_4 concentration in the reactor decreased to 77 mg/ℓ overnight. The graphs in Fig. 2 show that the reactor COD content decreased from an average value of about 1750 mg/ℓ to concentrations < 100 mg/ℓ. This observation can possibly be ascribed to the metal concentration in the feed water.

It has been reported that methanogenesis is stimulated by the addition of trace metals such as iron, cobalt and nickel (Speece 1996). Due to the relative high nickel concentration in the feed water, it can be hypostasised that the Methanogenic Bacteria (MB) rather than the SRB used the available COD. When considering the affinity of the SRB, the Acetogenic Bacteria (AB) and the MB for substrates such as acetate, CO_2 and H_2, it is evident that these groups of bacteria may out-compete each other for their preferred substrate. In the sulphate reducing stage, a complete reduction of sulphate to sulphide is desired. Channelling of reducing equivalents towards the SRB is enhanced by the ability of the SRB to effectively compete with other anaerobic bacteria for the available organic substrate and the sensitivity of other bacteria for sulphide (Lens *et al.,* 1998). Thus the anaerobic process can become very complex in the presence of sulphate and metals.

Determined	**Unit**	**Period**			
Period		1	2	3	4
HRT	h	24	12	12	24
Ratio's					
S/SO_4		0.13	0.22	0.24	0.16
Removal rates					
Vol. SO_4 rem. rate	g SO_4 (ℓ.d)	1.05	2.45	1.92	1.62
Spec. SO_4 rem. rate	g SO_4/g VSS	0.35	0.9	0.52	0.49

Table 5: The sulphate removal rates and experimental ratios

The sulphate removal rates and ratios as obtained during study 2 are presented in Table 5. The highest obtained sulphate removal rate was 2.45 g SO_4 (ℓ.d) at a HRT of 12 h. This result compared poorly with the results during study 1, when higher removal rates (2.9, 6.2, 8.4 g SO4/(ℓ.d)) were obtained partly due to shorter HRT (10, 5.3 and 4.3 h, respectively), partly to the metal concentration in the feed water during study 2 as well as to a more stable reactor system during study 1. The longer a biological reactor is in operation the more stable the process becomes, due to the adapted to sulphate removal biomass.

Study 3

The sulphate removal during study 3 is presented in Figure 3. It can be observed from the graphs in Figure 3 that during the first part of the study the sulphate concentration in the treated water was irregular, which improved on day 21. This improvement coincided with a faster feed rate to the reactor, which resulted in a lower HRT. Due to the higher sulphate load, the SRB became more competitive for the available carbon and energy source and thus possibly out-competed the MB.

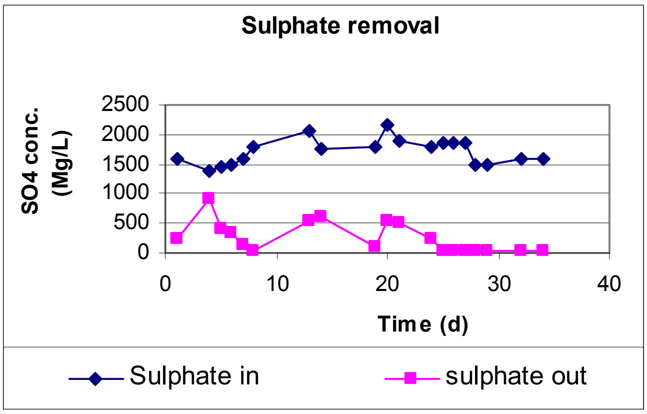

Figure 3: The sulphate concentration in the feed and treated water

The chemical compositions of the feed and the treated water as well as the sulphate removal rate are presented in Table 6. It can be observed from the data in Table 6 that the average removal rate was 1.70 g SO4/(ℓ.d), which was lower than the removal rates in studies 1 and 2. No immediate explanation can be provided for this result, except that the HRT was longer during study 3. Furthermore, the total experimental period was possibly too short during study 3, which was due to the unavailability of more mine effluent.

Parameter	**Feed water: AMD:Effluent=1:1**	**Treated water**
pH (units)	5.96	7.12
SO_4 (mg/ℓ)	1707	253
Suphide (mg/ℓ)	n.a	242
Removal rate (g SO4/(ℓ.d))	1.70	

Table 6: Chemical composition of feed and treated water during study 3

Sulphide production and the S^{2-}/SO_4 ratios

Sulphide is produced when sulphate is biologically reduced in the presence of an electron donor (reaction 1). The sulphide concentration as well as the S^{2-}/SO_4 ratios can be seen in Tables 4, 5 and 6, respectively. The experimental S^{2-}/SO_4 ratios varied between 0.15 and 0.20 (0.17, 0.18 and 0.17), while the theoretical (mass) ratio value is 0.33 (reaction 1).

$$2C_2H_5OH + 3SO_4^{2-} \rightarrow 3HS^- + 3HCO_3^- + 3H_2O + CO_2 \quad (1)$$

The lower experimental S_{2-}/SO_4 ratio values can partly be ascribed to Metal/Sulphide precipitation in the reactor. The produced sulphide, which remains in the treated water after metal sulphide precipitation, can chemically be converted to elemental sulphur (Maree et al., 2004b). The produced elemental sulphur can be sold to industry for the production of sulphuric acid, or can be sold to fertilizer producers. Since South Africa is a net importer of Sulphur, sulphur production is beneficial for the local economy.

Metal Removal

The produced sulphide after biological sulphate removal forms insoluble salts with the available metals in AMD. For this reason, the produced sulphide can be used to precipitate metals in AMD, *prior* to feeding AMD to the reactor. The formed metal sulphides will precipitate, which can be removed in a settler. In addition, the produced alkalinity in the treated water can neutralise the acidity present in AMD, thereby increasing the pH of the AMD. This improved AMD can be dosed to the biological sulphate removing reactor. The ratio AMD to treated water is dependent on the acidity in AMD and the alkalinity in the treated water, but can usually be maintained at 1:1. Recycling the effluent stream implicates the reintroduction of other substances such as the non-reduced sulphate in the treated water, however, this is often of no significance, as the sulphate removal efficiency is usually > 80% sulphate removed. Metals such as iron, copper, zinc and manganese will precipitate with sulphide at the operating pH.

Study 1

The metal concentration of AMD, the diluted with effluent AMD (1:1) as well as the treated AMD is presented in Table 7. The results show that the iron and copper concentration was < 0.05, while the aluminium, manganese and zinc concentrations decreased to less than 4 mg/ℓ. Aluminium precipitated as $Al(OH)_3$, while the other metals were removed as metal sulphides. These results show that iron and copper could be removed to the required concentrations through the presence of sulphide after sulphate reduction. The metal sulphides can be removed with the sludge. In case the metal concentration in the sludge is not too high, this sludge waste can be used as soil improver for agricultural purposes. In addition, the metal sulphide precipitate can be recycled to a metal recovery plant, to recover the precipitated metals, which can add value to the operations of the mine.

In case the metal concentration is too high for the allowable governmental set regulations, the sludge has to be disposed off in the tailings dams. The aluminium, manganese and zinc concentrations in the treated water as obtained in study 1 are too high for safely disposing the treated water in the environment, except when the stream can be diluted with a non metal containing stream.

Parameter (in mg/ℓ)	**AMD**	**Diluted AMD**	**Treated AMD**
Iron	139	0.06	0.04
Aluminium	11.7	5	3.5
Manganese	8.4	3.2	1.25
Copper	0.35	0.01	0.01
Zinc	113	3.1	3.1

Table 7: Metal concentration in AMD, in diluted AMD and in treated AMD

Study 2

The results are shown in Table 8.

Metal (Mg/ℓ)	**Feed 1**	**Feed 2**	**Period 1**	**Period 2**	**Period 3**	**Period 4**
Nickel	5.86	5.5	0.15	0.17	0.14	0.16
Zinc	1.25	38	0.03	0.03	0.03	0.03
Manganese	0.97	0.99	0.97	1.20	0.17	0.06
Copper	0.01	0.05	0.03	0.03	0.03	0.03

Table 8: The metal concentration in the feed and treated BCL mine water.

From the data in Table 8, it can be noted that the metals nickel, zinc, manganese and copper were present in the feed water at concentrations of 5-6 mg/ℓ, from 1-38 mg/ℓ, at about 1 mg/ℓ and less than 0.1 mg/ℓ, respectively. The Cu, Ni and Zn concentrations in the treated water were less than 1 mg/ℓ, during the first periods, while the Mn concentration did not decrease. However, during periods 3 and 4, the Mn concentration in the treated water was reduced to 0.17 and 0.06 mg/ℓ, which might be pH related as the reactor pH was higher at 7.00 and 7.55, respectively, during those latter periods. Although the zinc concentration in the feed was as high as 38 mg/ℓ, no zinc was analysed in the treated water, indicating that the produced sulphide precipitated all available zinc.

Study 3

The data in Table 9 show that most metals were removed after the biological treatment of AMD. Manganese remained in solution at a concentration of 0.3.

Metal (mg/ℓ)	**AMD**	**Treated water**
Al	< 0.07	n.a
Co	0.04	< 0.04
Fe	76	0.08
Mn	9.3	0.3
Zn	4	< 0.07
Ni	0.61	< 0.03

Table 9: Metal concentration in AMD and treated water

Metals as trace elements

Trace elements are present in low concentrations in rocks, soils, water and in the atmosphere. Some trace elements, such as cobalt, copper, zinc, iron and nickel are (micro-) nutrients. Trace metals play a structural role in various enzymes, which are the cells catalysts (Brock 1997). The activity of biomass is dependent upon a host of factors, but in the case of trace metals, the lack of only one can severely limit the overall process. Especially iron, cobalt, nickel and zinc have been shown to be stimulatory to the methanogens, while degrading acetate. Speece (1996) described the importance of three trace elements, being nickel, iron and cobalt.

When these three trace elements were directly injected into the reactor, during the described experiment, better acetate utilization rates could be observed immediately, as could the gas production. It might thus be possible that the elevated nickel (and likely the zinc) concentration in study 2, especially, played an important role in the enzyme activity of the methanogens, thus enabling the methanogens rather than the SRB to use the available COD, which explains the less efficient sulphate removal.

Metal toxicity

Mining is one of the oldest and most important activities of humankind, as can be assumed from a number of present sites in Europe, where underground mining for flint was being undertaken at several locations, e.g. Grimes grave, Norfolk, UK and Spiennes in Belgium (Holgate, 1991). By Bronze Age, mining was already beginning to disturb sulphide deposits that were capable of giving rise to polluted mine drainage. Evidence from sediment cores obtained from the Odiel-Tinto estuary in south western Spain clearly indicate the advent of water pollution due to mining activities during the Middle Bronze Age (Ruiz *et al*., 1998). Thus, the presence of (heavy) metals in the environment is a man made problem. Minerals are largely chemically stable under “in situ” geological conditions. In the mining industry, the release of metal ions results from the weathering of sulphide ores containing minerals. Metals show toxic effect to organisms in the natural water systems, which depends on many factors such as temperature, pH and water hardness. The negative effects of heavy metals range from lethal to decreased reproduction and life expectancy and often in a decrease in biotic diversity. Most metals tend to bio-accumulate in fish and thus carry the toxic effect on to the next level in the food chain, which implies that metal accumulation in fish can be harmful to humans eating the contaminated fish. Thus, metals have to be removed from waste waters and as shown in this study that can be achieved in most instances through the biological treatment on mine effluents, removing sulphate, metals and acidity.

CONCLUSIONS

The results of studies 1-3 showed that the sulphate, acidity and metal concentration in AMD can be treated applying the biological sulphate removal technology. It was shown that when the pH of the AMD is too low to feed directly to the biological reactor, the AMD can be diluted with the effluent of biologically treated water.

This way of treatment offers the following benefits: the pH of the water is increased to such values that the diluted AMD can safely be used as feed water for the biological process: the acidity in the AMD is neutralised by the alkalinity in the treated water: the reduction of sulphate produces sulphide, which, when present in the treated water, can precipitate the metals available in the AMD. It was shown in study 1 that when the reactor is in operation for a long time, the biomass becomes sulphate reducing specific. This implies that under those conditions, AMD with a $pH < 5$ can immediately be fed to the reactor as the produced alkalinity in the reactor can buffer the lower pH of the incoming AMD, used as feed water. Metal removal occurred in all three studies. It was shown that certain metals, such as nickel, zinc, cobalt and iron can stimulate the MB in the sulphidogenic reactor, which resulted in less COD available for the SRB and thus in a lower sulphate removal efficiency. Therefore the metals need to be removed, prior to feeding metal containing AMD to the biological reactor.

The metal concentration in the treated AMD was significantly reduced after the biological sulphate reduction, due to the metal sulphide precipitation. The metal containing sludge can be disposed off in the tailings dam or in case when the metal concentration is not too high, the metal containing sludge can be used for agricultural purposes. In that case a potential waste product can have beneficial added value. In addition, the metal sulphide precipitate can be recycled to a metal recovery plant, to recover the precipitated metals, which can add value to the operations of the mine.

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