

Acid Mine Water Reclamation using the ABC Process

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Abstract

The gold mines on which much of South Africa's wealth was founded are closed or closing. Mining concerns therefore have stopped pumping underground water from the mines which are filling with water (AMD) that is acidic, saline and vitiated with metals from iron to uranium. By 2002 the West Rand Basin's mines were all flooded and some 15 million litres of AMD started to decant each day. The acid mine drainage (AMD) of this area (region) is characterised by a pH of around 3 and by concentrations of about 2 to 4.5 g/L of sulphate, 250 to 1200 mg/L of Ferrous iron, 60 to 175 mg/L of Mn and 120 mg/L of Mg.

The CSIR ABC desalination process, developed for AMD neutralisation and the removal of total dissolved solids from 2 600 to 360 mg/L was demonstrated at a pilot plant. Metals were effectively removed through precipitation with CaS, Ca(HS)₂ or Ca(OH)₂. The tests showed that during pre-treatment, sulphate was lowered from 4 500 mg/L to 1 250 mg/L by gypsum crystallization; metals were precipitated to low values as either hydroxides or sulfides, depending on the precipitation agent used. The BaCO₃ treatment then lowered sulphate to less than 100 mg/L. The alkalinity of the calcium bicarbonate-rich water was reduced from 1 000 to 110 mg/L (as CaCO₃).

Raw materials for the water treatment stage were recovered through the sludge processing stage. CaS or Ca(HS)₂ was produced from the CaSO₄ sludge and BaCO₃ from the BaSO₄/CaCO₃ sludge.

Introduction

Although mining activities have been an important sector of the South African economy to date, many mines are now abandoned, threatening the environment specifically as water is not being pumped out of these closed or abandoned mines any longer and is converted to acid mine drainage (AMD). AMD forms when water comes into contact with the exposed ore body of coal and gold mines, leaving the water high in dissolved metals and sulphates. Rising water levels in these mines increases the risk of polluted water reaching porous rock and ultimately decanting at the surface.

South Africa is considered a semi-arid country and water has been identified as the country's most limiting natural resource (National State of the Environment Report, SA). Due to both South Africa's growing population and the need for social upliftment, the total water demand for agriculture, domestic use, industrialisation and mining has increased rapidly (Basson et al. 1997). Increasing stress is being placed on the

available water resources, demanding that water management efforts cannot only be directed at source level, but must also focus on the water re-use opportunities, i.e. industrial effluent treatment. The recovery of saleable products, generated during the treatment process, could also render the treatment technology more cost effective and economically attractive. For this reason the treatment and re-use of industrial and mining effluents can become a financially lucrative business with highly beneficial impacts on the environment.

The CSIR's ABC water treatment process is designed to achieve neutralisation as well as metal and sulphate removal from Acid Mine Drainage (AMD) by the optimal (efficient) use of readily available and affordable chemicals. The water stage is integrated with a sludge processing stage to recover alkali, barium and calcium (A,B,C) from the chemical sludge produced in the water treatment part of the process. Good quality water, suitable for re-use, is produced in a cost-effective way from polluted mine water through the recovery of by-products and reagents from the waste sludge. To conform with the principle of utilising waste as a renewable resource, the recycling of these initial reagents from sludge generated during the AMD water stage, forms an integral part of the ABC process. This creates a predominantly closed-loop treatment process which reduces the overall treatment costs.

This AMD treatment process was successfully operated, demonstrating that the CSIR ABC process can treat AMD water to meet drinking water quality standards and that raw materials needed for the water treatment stage can be recycled, reducing the associated treatment costs. Various options for AMD neutralisation were investigated including the use of precipitated CaCO_3 , a by-product from the paper industry and Ca(OH)_2 recovered from the thermal sludge processing stage. CaS , also recovered during sludge processing, is used for metal removal and further neutralization while metal hydroxides are removed at high pH through additional dosing of Ca(OH)_2 . Either BaS or BaCO_3 can be used for the final sulphate removal step. BaCO_3 was selected as it does not require H_2S stripping from the main water stream, but from a concentrated stream in the sludge processing stage.

Although decanting AMD represents a serious environmental challenge, especially in South Africa, the ABC process offers a sustainable solution for its remediation that can also be implemented in other countries facing challenges associated with AMD. This technology provides an effective solution with which to address the serious environmental challenges inadvertently caused by mining activities of the previous century.

Materials and Methods

Feedstock

Acid mine water containing 2 000 (low sulphate AMD) to 4 500 (high sulphate AMD) mg/L sulphate was pumped directly from a gold mine shaft in the Western Basin to the $1\text{m}^3/\text{h}$ ABC pilot plant. Barium carbonate was used for sulphate removal and the process was operated in continuous mode.

Equipment

A pilot plant was constructed for treatment of the water. Pre-treatment with CaCO_3 , lime or CaS for removal of free acid and metals, lime treatment for removal of magnesium and partial removal of sulphate, and sulphate removal with BaCO_3 were studied by dosing combinations CaCO_3 , lime, CaS and BaCO_3 to the plant. Sludges (metal hydroxides, gypsum/ $\text{Mg}(\text{OH})_2$ and $\text{BaSO}_4/\text{CaCO}_3$) were collected and treated in batch operation for dewatering, drying and thermal reduction in a kiln.

Experimental procedure

Water was fed continuously for 24 h/day, 7 days/week. Samples were collected and analyzed on-site for pH, sulphate, calcium, magnesium and iron(II). Sludge were withdrawn continuously from the clarifiers and stored for further batch processing.

Experimental programme

During water treatment the following parameters were varied to study their effects:

- Chemical reagent for pre-treatment (CaCO_3 , Lime or CaS)
- Effect of pH on Ni and Co precipitation (6.0, 7.0, 8.0)
- Effect of sludge recirculation on metal precipitation and gypsum crystallization.
- Reactor type for sulphate removal with BaCO_3 (complete-mix reactor, fluidized-bed reactor)

Analytical procedure

Water samples were collected at various stages in the treatment process and filtered through Whatman No 1 filter paper prior to sulphate, alkalinity, calcium, and Fe (II) analysis. Suspended solids (SS), acidity, and pH determinations were carried out using standard procedures (APHA, 1989). Acidity was determined by titration to pH 8.3 using a 0.1 N NaOH solution. Sulphide (a product from the thermal studies) was determined by mortaring and dissolving 0.5 g of the product in 100 ml deionized water followed by the iodine method for sulphide analysis (APHA, 1989). Metals were determined with an atomic absorption spectrometer (SpectraAA 220FS, Varian Techtron Pty. LTD Springvale, Austria);

Results and Discussion

Water Treatment Stage

Water Quality

Table 1 shows the chemical composition of the water of the low sulphate AMD feed and treated water. The Total Dissolved Solids (TDS) content was reduced from 2 640 mg/L in the feed water to 360 mg/L in the treated water. During CaCO_3 treatment free acid of 370 mg/L was removed as indicated by the increase in the pH from 3.3 to 5.8. Iron(III) and aluminium(III) were removed to concentrations below 1 mg/L.

Table 1. Chemical composition of feed and treated water for the low sulphate AMD

Parameter		Low sulphate water		Recom- mended
		Feed	Treated	
pH		3.3	7.9	
Alkalinity	(mg/L as CaCO ₃)	0	140	
Sulphate	(mg/L as SO ₄)	1910	90	500
Chloride	(mg/L as Cl)	44.46	49.52	200
Fluoride	(mg/L as F)	5.40	0.07	
Ammonia N	(mg/L as N)	0.76	0.64	
Nitrate	(mg/L as N)	0.41	0.46	
Sodium	(mg/L as Na)	46.48	53.28	150
Potassium	(mg/L as K)	4.38	4.80	
Magnesium	(mg/L as Mg)	124.61	0.98	
Calcium	(mg/L as Ca)	205.00	75.00	
Barium	(mg/L as Ba)	0.20	0.50	
Silica	(mg/L as Si)	11.00	0.45	
Manganese	(mg/L as Mn)	63.69	0.09	1
Total acidity	(mg/L as CaCO ₃)	714.16	0.59	
Free acidity	(mg/L as CaCO ₃)	370.00	0.00	
Iron (II)	(mg/L as Fe)	180.00	0.30	1
Iron (III)	(mg/L as Fe)	2.00	0.00	0
Aluminium	(mg/L as Al)	2.97	0.01	1
Chromium	(mg/L as Cr)	0.26	0.00	
Zinc	(mg/L as Zn)	3.20	0.06	0.05
Copper	(mg/L as Cu)	21.00	0.02	
Cobalt	(mg/L as Co)	2.05	0.02	0.01
Nickel	(mg/L as Ni)	5.60	0.01	0.01
Lead	(mg/L as Pb)	0.03	0.01	
Uranium	(ug/L as U)	465	20	
TDS	(mg/L)	2640	360	

Metal removal

During neutralisation and metal removal (pre-treatment stage using CaCO₃, Ca(OH)₂ or CaS), bivalent metals Fe, Ni and Co, were removed to concentrations less than 0.5 mg/L. Mn was removed to less than 4 mg/L. This was achieved due to the low solubility-products for FeS (17.3 mg/L), MnS (14.96 mg/L) and NiS (20.7 mg/L) (Sillen & Martell, 1964). Metals should be removed separately from gypsum to allow for easier recovery of valuable metals such as nickel and cobalt and also to facilitate higher yields during the processing of gypsum to CaS.

The subsequent lime treatment (magnesium removal and partial gypsum crystallisation stage) resulted in magnesium concentrations lowered from 145 to 1 mg/L and sulphate concentration from 1 910 mg/L (as SO₄) to between 1 600 and 1 900 mg/L. Mn was also removed to less than 1 mg/L during this lime treatment stage.

Sulphate removal

Sulphate is removed as gypsum (CaSO₄) in the pre-treatment (magnesium removal and gypsum crystallisation stage) and as BaSO₄ in the BaCO₃ treatment stage. Whereas gypsum is normally soluble below 1 500 mgSO₄/L, this concentration is increased by counter-ions, e.g Mg²⁺ and Na²⁺ in solution. The kinetics of gypsum precipitation also plays an important role in sulphate removal *via* gypsum. However, BaSO₄ has limited solubility allowing complete sulphate removal.

During the BaCO₃ treatment stage, the pH was adjusted from 11.5 to 8.4 with CO₂. Ca²⁺ concentration was reduced from 205 to 75 mg/L due to CaCO₃-precipitation. The sulphate concentration was reduced from 1 600 to around 10 mg/L. Final

effluent was contacted with sulphate-rich water to precipitate any residual barium ions. The concentrations to which sulphate and metals are removed are governed by the solubility products of the various compounds. Good results were also achieved when the high sulphate AMD water with a sulphate concentration of 4 500 mg/L was treated (Table 2).

Table 2. The water quality before and after the various treatment stages for the high sulphate AMD

Parameter		Water quality						
		Feed	CaCO ₃ neutrali	CaS dosage	Lime dosage	CO ₂ dosage	BaCO ₃ addition	SO ₄ addition
pH		2.9	5.8	6.8	10.9	8.4	8.5	8.3
Sulphate	(mg/L as SO ₄)	4870	4710	4500	2300	2310	85	200
Chloride	(mg/L as Cl)	37	37	37	37	37	37	37
Alkalinity	(mg/L as CaCO ₃)	0.00			300	60	65	63
Acidity	(mg/L as CaCO ₃)	800	100	50				
Sodium	(mg/L as Na)	50	50	50	50	50	50	50
Magnesium	(mg/L as Mg)	147	148	146	10	10	10	10
Calcium	(mg/L as Ca)	613	920	1580	1040	948	10	70
Barium	(mg/L as Ba)						40	0.4
Manganese	(mg/L as Mn)	46	46	4.8	1.0			
Iron (II)	(mg/L as Fe)	949	949	11	0.01			
Iron (III)	(mg/L as Fe)	35	0	0	0			
Aluminium	(mg/L as Al)	26.4	0.5					
Cobalt	(mg/L as Co)	5	5	0.06				
Nickel	(mg/L as Ni)	18	18	0.14				
Zinc	(mg/L as Zn)	11.9	11.9	0.15				
TDS	mg/L	7592	6993	6378	3660	3399	280	414
Cations	meq/L	102.5	99.2	94.8	55	50.4	4.1	6.5
Anions	meq/L	102.5	99.2	94.8	55	50.4	4.1	6.5

Note: Ca & SO₄ values adjusted to obtain ion balance

Barium Sludge Processing Stage

A filter press dewatering system was used to reduce the volume and weight of the slurry waste or process stream. The dewatered spent sludge (filter cake) from the BaCO₃ sulphate removal stage (barium reactor) was subjected to thermal reduction and chemical treatment to regenerate barium carbonate for re-use of barium in the BaCO₃ sulphate removal stage. The process also generated calcium hydroxide which is re-used in the first part of the water treatment process and hydrogen sulphide. Hydrogen sulphide (H₂S) can be used in the water treatment plant to precipitate metals as metal sulfides or be converted and sold as a source of sulphur or sulphuric acid (H₂SO₄).

Thermal Reduction

The barium sludge from the water treatment stage comprises a mixture of barium sulphate (BaSO₄) and calcium carbonate (CaCO₃). The dried filter cake from the dewater plant was mixed with powdered coal and fed to a kiln which operates at 1100 °C in a reducing environment provided by the coal. The barium sulphate (BaSO₄) was converted to barium sulphide (BaS). In addition, the calcium carbonate (CaCO₃) decomposed to produce calcium oxide (CaO). The carbon dioxide (CO₂) rich kiln off-gas was used as the source of carbon dioxide for the barium carbonation reaction.

Barium/Calcium Separation

The mixture of barium sulphide (BaS) and calcium oxide (CaO) from the kiln, together with some ash were slurried (10 %) with a mixture of recycled and final effluent water. The barium sulphide dissolved, while the calcium oxide reacted with water to produce calcium hydroxide, which has a limited solubility and was separated from the aqueous barium species by settling. The Ca(OH)_2 cake was returned to the water treatment stage for re-use. The ash (from the coal) remains as a contaminant in the calcium hydroxide and leaves the water treatment system with the sludge.

Barium Carbonation & Sulphur production

The filtered barium sulphide (BaS) solution was fed into a reactor where it was contacted with the CO_2 rich kiln off-gas and the aqueous barium sulphide reacted with the carbon dioxide to yield barium carbonate, which has a very low solubility and therefore precipitates. The carbonation reaction produces a by-product, a gas stream rich in hydrogen sulphide (H_2S). The hydrogen sulphide was reacted with lime to generate calcium sulphide for metal removal in the water treatment stage. Alternatively, the hydrogen sulphide can be used as a feed stream for sulphur or sulphuric acid production.

Conclusions

- The CSIR ABC (Alkali-Barium-Calcium) desalination process can be used for neutralisation of AMD and lowering the total dissolved solids from 2 600 to 360 mg/L.
- Metals can be removed effectively through precipitation with lime, CaS, or Ca(HS)_2 .
- Sulphate can be removed to values less than 100 mg/L through BaSO_4 precipitation using BaCO_3 as precipitant.
- Raw materials, namely CaS, Ca(OH)_2 and BaCO_3 needed for the water treatment stages were recovered from the sludge processing stage

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