Neutralization of acid leachate at a nickel mine with limestone

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Abstract
Pyrites-rich discard is produced as waste during mineral processing. During oxidation of pyrites in a tailings dam, acid leachate is produced which contains high concentrations of acid, sulphate and metals. In this paper an integrated approach is proposed for dealing with the treatment of discard leachate. The approach consists of the following stages: $CaCO_3$ handling and dosing; $CaCO_3$-neutralization; and gypsum crystallization to achieve partial sulphate removal. The following conclusions were made during the investigation: (i) Powdered calcium carbonate placed in a pile can be slurried to a constant density and applied for treatment of acid water; (ii) Acid water can be treated with calcium carbonate for neutralization and removal of metals (e.g. iron(II)).

Key words: Discard leachate, calcium carbonate, limestone, gypsum crystallization.

Introduction

Mine waste discard, that contains pyrites, is produced as a waste during mining operations. When pyrites-rich waste ore is exposed to oxygen and water in the presence of iron oxidising bacteria, acid leachate is produced which contains high concentrations of acid, sulphate and metals due to oxidation of pyrites (Reaction 1).

$$2FeS_2 + 7½O_2 + H_2O \rightarrow Fe_2(SO_4)_3 + H_2SO_4 \quad (1)$$

BCL Limited, a copper-nickel mine in Botswana, mines and processes 450 t/d of ore and experiences such a problem. The operations consist of underground mining, concentration of the copper and nickel part of the ore by means of flotation, and smelting of the concentrate to produce copper and nickel. The main flows of water into the underground workings include cooling water (with high NaCl content from the ice plant), groundwater (fissure water) and water recycled with the coarse waste backfill. These streams are currently mixed and returned to surface where the combined stream of 350 m^3/h is neutralised.

Central to the water network is the Mill Return water Sump (MRWS). The used-water streams are recycled to the MRWS, from where the concentrator circuit is supplied with water. Lime is used to adjust the pH of the return water to 8.5 in the MRWS. This water is used in the concentrator circuit as transport medium and to facilitate separation. The pH of the water is the main quality consideration for the concentrator - high salinity levels do not pose a problem. In the copper-nickel concentration processing plant, solid waste material containing 5% pyrite is produced. The coarse fraction of the solid waste material is discarded as backfill underground, while the fine waste is discharged onto a tailings waste dump. These wastes give rise to acidic leachate due to pyrite oxidation. Lime is used to neutralise 350 m^3/h of underground mine water (with an acidity of 235 mg/l as $CaCO_3$) and 60 m^3/h of tailings dump seepage (with an acidity of 5000 mg/l as $CaCO_3$). Excess water is used for the cooling and granulation circuit in the smelter. The smelter intake water chloride concentration should be limited to 5 mg/l to prevent pitting corrosion in the smelter cooling jackets so for this purpose raw water is imported from a local dam.

BCL currently experiences the following water-related problems:

- Neutralised water is discharged into a public stream at a rate of 300 m^3/h. The effluent quality does not meet the permitted level of 500 mg/l sulphate.

- The neutralisation cost is high due to the use of imported lime.
- Excessive acid seepage has resulted in deterioration of the land area adjacent to the tailings dump.
- The water intake of 300 to 400 m^3/h is expensive.

A modelling exercise was carried out during 1999 to audit and simulate the water network of BCL with the aim to identify the optimum water management strategy (van Tonder, *et al*, 2000). It was found that discard leachate could be neutralized with limestone to minimise chemical cost and that it should be treated, before being mixed with less polluted streams, to achieve maximum sulphate removal through gypsum crystallization and precipitation. The latter will result in reduced scaling of gypsum in the metallurgical plant.

The purpose of this study was to:

- Determine through laboratory studies, pilot-scale studies and full-scale experience gained at Navigation Section of Landau Colliery the most suitable effluent treatment configuration for neutralization of discard leachate at BCL. An integrated process existing of the following stages was investigated: $CaCO_3$ handling and dosing; $CaCO_3$-neutralization; and gypsum crystallization to achieve partial sulphate removal.
- Develop design criteria for the construction of a plant to treat 50 m^3/h of discard leachate.

Materials and methods

Feedstock. Powdered calcium carbonate, a by-product from the paper industry, was used for neutralization of acid water. It contained 25% moisture and 10% impurities (dry mass) which was mainly silica. Coal discard leachate or a synthetic solution of similar chemical composition was used as feed water for studies on iron(II)-oxidation at low pH and $CaCO_3$ neutralization.

Equipment. The three stages of the integrated process were studied separately.

The *$CaCO_3$ - handling and dosing system* (Photograph 1) was evaluated on the first full-scale plant of its kind. It has a capacity of 23 t/d $CaCO_3$. The plant consists of the following:

- A sloped concrete slab onto which the $CaCO_3$ powder is dumped and stored. The $CaCO_3$ powder is slurried with a water jet and collected in a slurry tank through gravity flow.
- Float valve in the slurry tank to maintain the water level at a specific height.
- $CaCO_3$- recycle slurry pump that withdraws slurried $CaCO_3$ from the slurry tank or clear water through a water jet onto the $CaCO_3$ dump to maintain a constant $CaCO_3$ concentration. The slurried $CaCO_3$ is returned by gravity via the sloped concrete slab back to the slurry tank. The $CaCO_3$ concentration is controlled by a density meter, which directs the water jet on to the $CaCO_3$ dump when the slurry density is below a set value and onto a clean section of the slab when the density is equal to or above the set slurry density. A side-stream from the delivery side of the recycle pump is passed through the density meter. The density meter works on the basis where the mass of a fixed slurry volume is measured on a continuous basis with a load cell.
- Transfer pump, feeding slurried $CaCO_3$ to the neutralization reactor.

Iron(II)-oxidation at low pH was studied by doing laboratory studies under batch conditions. The solutions in the beaker reactors were stirred continuously and aerated with compressed air through diffusers (porosity no. 2, 210 x 8mm (OD)). The air to the container reactors and box reactors was distributed through small holes punched into a perspex pipe situated at the bottom of the reactor. Varius support media were evaluated to identify the most suitable medium for iron(II)-oxidation at low pH. Photo 1 shows Geotextile as support medium.

The *$CaCO_3$ neutralization stage* consisted of a fluidised-bed reactor with a sludge separator. The $CaCO_3$-neutralization stage was a continuous laboratory-scale plant. The dimensions are indicated in Table 1. Compressed air was used for iron(II) oxidation

when powder $CaCO_3$ was used for neutralization..

Table 1. Dimensions of $CaCO_3$ neutralization pilot plant.

Parameter	Value	
	Fluidised-bed	Solids separation
Feed rate (l/h)	24	
Recycle rate (l/h)	200	
Diameter (m)	0.20	0.53
Water height (m)	4.99	0.35
Specific surface area (m^2/m^3)	20.2	-
Up-flow velocity (m/h)	6.37	0.91
Residence time (h)	6.53	3.22

Experimental. The performance of the various stages (iron(II)-oxidation and $CaCO_3$ neutralization) were evaluated by determining the chemical composition of the feed and treated water during batch experiments and during continuous operation.

Batch studies were carried out in beakers at atmospheric pressure to determine the rate of iron(II) biological oxidation. The following steps were followed:

- Water in the reactor was replaced with new feed water. The same Support medium was used repeatedly during consecutive batch runs. During the first run the reactor was inoculated by adding 5% discard leachate from Navigation Mine to the volume of the beaker.
- Samples were taken at different intervals, filtered and analyzed for iron(II) concentration and pH (beginning and end of the experiment).
- The run was stopped when iron(II) was completely removed.
- The procedure was repeated for several iterations until the rate of iron(II)-oxidation had stabilized.

Analytical. Samples were collected regularly and filtered through Whatman No 1 filter paper. Sulphate, sulphide, alkalinity, calcium, iron(II), mixed liquor suspended solids (MLSS), volatile suspended solids (VSS), acidity and pH determinations were carried out manually according to procedures described in Standard Methods (APHA, 1985). Calcium was analysed using atomic absorption spectrophotometry. Acidity was determined by titrating the solution to pH 8.3 using NaOH. The COD samples were pre-treated with a few drops of H_2SO_4 and N_2 to strip off H_2S gas.

Results and discussion

$CaCO_3$ handling and dosing system

Waste $CaCO_3$ from the paper industry was used for neutralization of acid water in the Primary Neutralization plant at Navigation since July 2001 and for neutralization of acid leached from the coal in the Coal Processing Plant since 12 June 2002 (Strobos, *et al*., 2002). During the first 12 months of operation the limestone throughput was limited to 2.5 t/d as only the Primary Neutralization Plant was served with limestone. Since July 2002, the throughput was increased to 20 t/d as limestone was also used to neutralize acid leached from the Coal Processing Plant. During operation of the Limestone plant at a high through-put of 20 t/d it was learned that the following operational guidelines need to be followed to allow smooth operation:

- Slurry limestone on slab to run-off completely into the slurry tank. No obstacles (e.g. sieves) should be positioned on the slab with the aim to separate stones from the fine particles) as it work against the slurry process. Such obstacles place a limit on the slurry density. A slurry density of only 1.09 can be achieved with sieves on the slab while a density of 1.5 would be required once the through-put has increased to the designed rate of 40 t/d (when discard leachate plant is in operation).
- The density of the limestone slurry needs to be monitored and controlled on a continuous basis. A density meter was developed for this purpose, as described under Materials and Methods.
- Stones need to be separated completely from the limestone to prevent blockages in the slurry pipelines and in the nozzles.

Iron(II)-oxidation at low pH

Figure 1 shows the rate of iron(II) removal at low pH with brown Geotextile as medium (Nengovhela, *et a.l*, 2002). It is noted that the rate of iron(II)-oxidation stabilised after 14 repeated batch studies. Bacterial growth has increased to the level where further bacterial growth is controlled by the available surface area of the Geotextile, oxygen in solution and the temperature. A maximum rate of 16.1 g Fe/(l.d) was determined for iron(II)-oxidation with Geotextile as medium. This is significantly higher than achieved with other support media (after 8 repeated batch studies) (Table 2). Du Preez and Maree (1994) showed that the rate of iron(II) oxidation is related to the surface area of the medium.

CaCO3-neutralization, Iron(II)-oxidation and Gypsum crystallization at neutral pH

Limestone can be used in the integrated process for treatment of acid water (Maree, 1997). In this process powdered $CaCO_3$ is used for iron(II)-oxidation at pH 5.5, neutralization, metal precipitation (e.g. Fe^{3+} and Al^{3+}) and gypsum crystallization, in the same reactor. The novelty of this development lies in the fact that conditions were identified where iron(II) can be oxidized at pH 5.5, by the addition of $CaCO_3$. Previously, lime was used to raise the pH to 7.2 where the rate of iron(II)-oxidation is rapid. Table 3 shows the results obtained when synthetic discard leachate was treated with limestone. The water was neutralized effectively and sulphate was reduced from 8 342 to 1 969 mg/l (as SO_4) (Maree *et al.*, 1998). It was possible to achieve complete iron(II) oxidation by using only $CaCO_3$ as the neutralization agent.

It was determined that the rate of iron(II)-oxidation is not only influenced by the iron(II), hydroxide and oxygen concentrations as suggested by Stumm and Lee (1961), but also by the suspended solids concentration as suggested by Maree *et al.* (1998). In order to achieve complete iron(II) oxidation sufficient reaction time was allowed for gypsum crystallization to reach its saturation level (2 h). Aeration and sludge recirculation were applied to maintain a suspended solids concentration at 50 g/l.

Table 2. Comparison between support media (pH=2.5; after 8 repeated batch studies)

Support medium	Iron(II)-oxidation rate (g Fe/(l.d))
Control	1.44
Rings (100g/l)	1.68
Pellets(100g/l)	2.64
Discard(100g/l)	2.88
Sand(100g/l)	4.32
Anthracite(100g/l)	4.49
Activated Carbon (100 g/l)	5.16
White geotextile (100 g/l)	6.25
Brown geotextile (100 g/l)	6.34
Grey geotextile (100 g/l)	6.98

Table 3. Chemical composition of feed (synthetic discard leachate) and $CaCO_3$ treated water.

Parameter	Feed	Treated
pH	1.8	6.6
Acidity (mg/l $CaCO_3$)	7 300	100
Sulphate (mg/l SO_4)	8 342	1 969
Ortho phosphate (mg/l P)	2.9	0.0
Chloride (mg/l Cl)	27	30
Iron(II) (mg/l Fe)	2 500	<56
Total iron (mg/l Fe)	2 500	<56

Full-scale plant

The information discussed above was used for the design of the BCL plant with a capacity of 50 m^3/d. The design was required to be flexible so that either crushed limestone, powder limestone or a mixture thereof could be used, depending on the availability of limestone and the iron(II)-concentration of the feed water. The process consists of the following stages:

- $CaCO_3$ handling and dosing system.
- Biological iron(II)-oxidation stage. Initially water with a low iron(II)-concentration (red lake) will be used as feed water. Red lake water contains only 100 mg/l iron(II) due to natural oxidation while stored for several months in the red lake. Trench water will be fed later directly to the neutralization plant and the red lake will be used for storage of waste.

This reactor is designed to treat a small stream of trench water to obtain design criteria for treatment of the total stream.

- Fluidised-bed reactor for neutralization of acid water with crushed limestone. No aeration is provided in this reactor as crushed limestone particles get scaled with gypsum and ferric hydroxide in the presence of aeration.
- Complete-mix reactor and thickener for limestone neutralization with powder $CaCO_3$, iron(II)-oxidation and gypsum crystallization.

Table 4 shows the dimensions of the various stages of the plant. The construction of this plant is complete and it has been commissioned during November 2002 (Photo's 2 to 7).

The treatment approach offers the following benefits:

- The least expensive alkali, chrushed limestone, is used for neutralization of the acid.
- Removal of the bulk of the sulphate concentration through gypsum crystallization.
- Reduced scaling in the metallurgical plant due to separate treatment of discard leachate to the level where it is saturated with respect to gypsum.

Table 5 shows results collected during commissioning of the plant when red lake water (low iron(II) concentration of 100 mg/l) was used as feed water. It is noted that:

- Acidity was reduced from 2 100 to 50 mg/l (as $CaCO_3$).
- PH was raised from 1.9 to 6.6.
- Iron(II) was removed from 100 mg/l to <20 mg/l (as Fe).

Conclusions

The following conclusions followed from the investigation:

- Powdered calcium carbonate in a dump can be slurried to a constant density and applied in the treatment of acid water.
- Acid water, rich in iron(II), can be treated with calcium carbonate for neutralization and, removal of metals (e.g. iron(II)).

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Photo 1. **Geotextile mounted on a perspex plate**

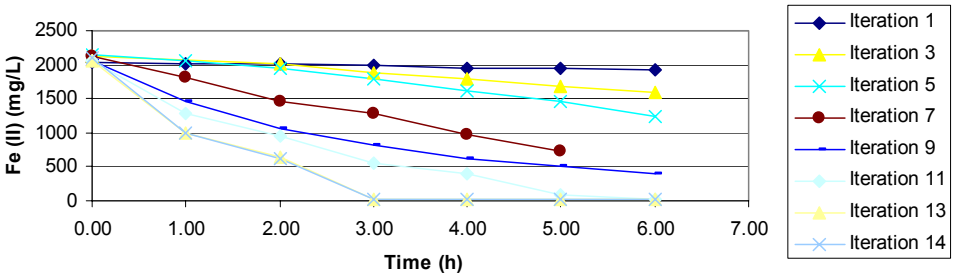

Figure 1. **Effect of Iteration on the rate of iron(II)-oxidation using brown geotextile.**

2. Red lake

3. Limestone handling and dosing system.

4. Limestone slurry tank, feed and recycle pumps

5. Iron(II)-oxidation and Fluidised-bed reactors

6. Complete-mix reactor for gypsum crystallization

7. Thickener

Photo's 2 to 7. Limestone neutralization plant at BCL, Botswana

Table 4. Dimensions of the various stages of the integrated limestone neutralization process.

Parameter	Stage				
	Iron(II)-oxidation	Limestone neutralization		Gypsum crystallization	Solids separation
		Column section	Cone section		
Flowrate (m^3/h)	50.0	50.0	50.0	50.0	50.0
Length (m)	3.2	9.3	2.4	10.0	15.0
Width (m)	3.2			5.0	5.0
Diameter (top) (m)		1.9	4.6		
Diameter (bottom) (m)		1.9	1.9		
Height (m)	4.0	9.3	2.4	4.0	3.4
Area (m^2)	10.0	2.7	16.6	50.6	75.0
Volume (m^3)	40.0	25.0	39.6	202.5	255.0
HRT (h)	0.8	0.5	0.8	4.1	3.8
Upflow velocity (m/h)		18.6	3.0		0.7

Table 5. Chemical composition of feed and treated water.

Parameter	Feed	Treated
Flow rate (m^3/h)	50	50
pH	1.9	6.6
Acidity (mg/l $CaCO_3$)	2 100	50
Iron(II) (mg/l Fe)	100	<20