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Continuous pilot scale assessment of the alkaline barium calcium desalination process for acid mine drainage treatment

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The alkaline barium calcium (ABC) desalination process for acid mine drainage treatment was evaluated at pilot scale. Experimental continuous sulphate removal was performed and regeneration of barium carbonates from barium sulphide/calcium carbonate sludge was conducted by using CO_2 gas at room temperature. The effect of process parameters was evaluated and it has been shown that it is possible to remove sulphate to very low levels in continuous mode using barium carbonate. Sulphate was removed from 2250 to 200 mg/L in 90 min using a Ba^{2+} to SO_4^{2-} molar ratio of 1:1. When the removal process was carried out for longer than 90 min a residual SO_4^{2-} concentration of 100 mg/L remained in the treated water using a Ba^{2+} to SO_4^{2-} molar ratio of 1:1, and this residual SO_4^{2-} lies within acceptable drinking water limit of 400 mg/L and also ensures that no residual toxic barium is present in the treated water. Moreover; the regenerative barium carbonate process, involving the conversion of BaS to $BaCO_3$ in the carbonation step has been assessed. The production of $BaCO_3$ and H_2S by treating aqueous slurry of BaS with CO_2 was also evaluated. The CO_2 flow rate had an impact on the $BaCO_3$ morphology. $BaCO_3$ was recovered from the pilot scale bubbling column reactor using 5% BaS at a CO_2 flow rate of 14.4 m^3/day and demonstrated effective sulphate removal ability during AMD treatment compared to commercial $BaCO_3$. The quality of barium carbonate generated was also preliminary assessed.

Introduction

One of the major challenges of mining and mineral processing is the generation of acid mine drainage (AMD) which if not managed can contaminate ground and surface water, affect the health of nearby communities as well as the environment [1,2]. AMD is produced when sulphate bearing minerals, are exposed to oxygen. The process, termed pyrite oxidation, is enhanced when water moves through and over the surfaces of acid bearing rock having been exposed as a result of mining activities that disturbed the underlying geology. AMD is generally characterized by one or more of the following: low pH, high total dissolved solids (TDS), high sulphates (SO_4), and/or high levels of heavy metals – particularly iron (Fe), manganese (Mn), nickel (Ni) and/or cobalt (Co). Heavy metals (and in some instances radioactivity) being mobilized at low pH, and elevated salt levels can pose a risk to human health and to the integrity of the aquatic ecosystem while also having a significant negative economic impact [3]. It is therefore imperative that mine waters be treated through processes which will address their low pH, high acidity and high metals content. But the challenge is that most treatment technologies are either inadequate or too expensive [4]. A wide range of AMD treatment technologies has been developed and globally proven [1,5]. Zhuang [5] has reviewed more than 85 patents on acid rock drainage treatment (ARD), filed since 2000 and classified ARD treatment into chemical precipitation process, adsorption method, biological system and passive treatment. However, in South Africa, very few of these technologies have indeed been successfully considered; with subsequent sludge or brine treatment requirements presenting major draw backs on their widespread commercial application. For instance the limestone and lime neutralization treatment technology has been successful in neutralizing AMD and is widely accepted as the leading AMD pre-treatment technology thus far. However, the process only reduces the sulphate content in the AMD to ±1200 mg/L after treatment while increasing the AMD pH to ±7 [6]. Some of the advantages of this process are the safe reagents handling, and simple process design with reduced capital and operation costs. However the limit to which sulphate can be removed from the mine water (~1200 mg/L) is still above the recommended discharge concentration of 400 mg/L [6]. A second stage is normally required to reduce the levels of sulphate to the legal limit of 400 mg/L before the water can be discharged to the national water network. A technology that has been considered for reducing the salt in particular sulphate to nearly zero is the reverse

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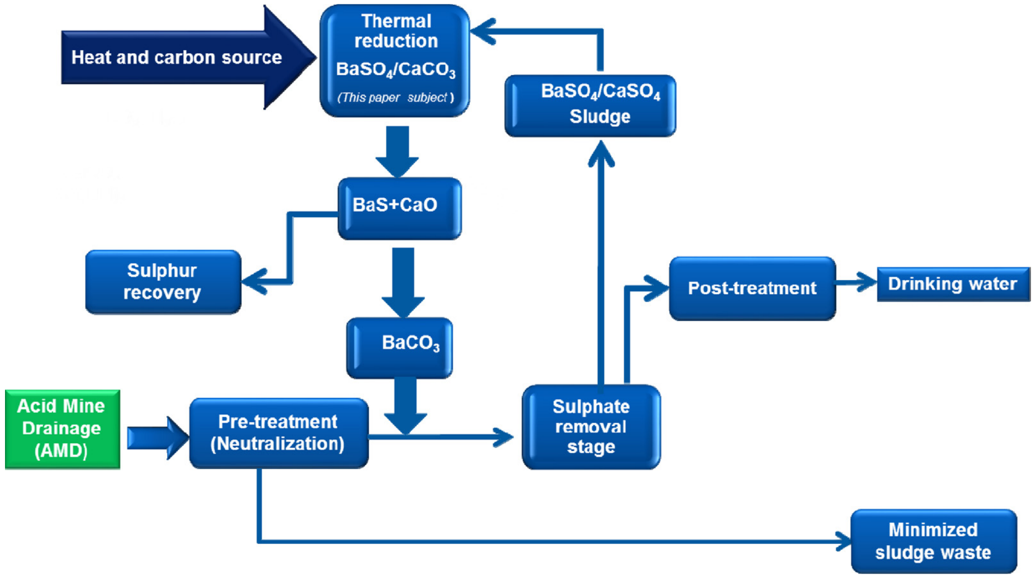

Fig. 1. Schematic diagram of the ABC chemical desalination technology.

osmosis (RO). However, the inherent drawback of RO technology is the production of large quantities of waste in the form of brine that need to be further processed or disposed of as well as the energy input. Recently a new chemical treatment process called the CSIR ABC process has been developed and is not only able to reduce the level of sulphate from pre-treated AMD to very low levels but integrate a sludge processing module for treatment and recycling of sludges generated, resulting in a near zero waste process. Several workers have described and applied the ABC treatment technology to recover drinking water and valuable by-products [1,7,8]. The ABC process was designed not only for AMD neutralization but for removing metals and sulphate as well. It is basically an integrated lime/limestone process combined with sulphate removal using barium carbonate ($BaCO_3$). The major improvement in this process is that the water-processing stage is integrated with a sludge-processing stage to recover barium carbonate and lime with the aim of an overall new low-waste technology.

The ABC treatment process has three stages as shown in Fig. 1:

- Neutralization and metal removal stage (stage 1);
- Sulphate removal stage using $BaCO_3$ (stage 2);
- Sludge processing stage (stage 3).

The barium sulphate-rich sludge from stage 2 is thermally reduced to water-soluble barium sulphide (BaS) using coal in a kiln at 1000 °C. The BaS is hydrolysed in hot water and carbonated with CO_2 to regenerate $BaCO_3$ which is re-used and this way kept in circulation through cycles.

This paper considers the continuous operation of the ABC technology at pilot scale to treat coal mines AMD and particularly assess the sludge processing stage. The effect of process parameters has been evaluated and it has been shown it is possible to remove sulphate to very low levels but also to control the properties (quality) of the barium carbonate regenerated via key process conditions.

Anglo coal with its partner BHP Billiton has recently implemented in South Africa a reverse osmosis (RO) plant to treat AMD from coal mines to potable standards. The process involves a pre-treatment stage where heavy metals are precipitated with increase of pH, and then the water from the pre-treatment stage is sent through a series of membranes for high recovery desalination process using the HiPRO process package with multistage UF/RO with a water recovery rate in excess of 99.7% [11]. However; some of the major drawbacks of the RO technology are: (a) the generation of a sodium sulphate rich brine streams which is quite expensive in terms of treatment and disposal. The actual waste disposal facilities account for 20–25% of the capital development cost and have a limited lifespan, which need to be extended every 4–5 years at a significant cost and (b) the brine produced often has a total dissolved solids (TDS) concentration of between 20,000 and 35,000 mg/L [11]. The high salinity of the brine makes discharge to sewer and surface irrigation unfeasible.

Preliminary techno-economic studies from previous works [9,10] showed that a RO process plant with a capacity of 20 ML/day of AMD water will require a capital cost comparable to a plant using the CSIR ABC process. A preliminary economic analysis of a 20 ML/day ABC desalination process is shown in Table 1. However; while the ABC process may be able to generate extra value from the selling of sulphur generated during the sludge processing stage, the RO process does not have a viable treatment option for the

Table 1
Preliminary economic analysis of ABC desalination process.

	Value
A. Feed water	
Feed water:	
Flow (ML/d)	20
Sodium	41.7
Chloride	47.3
Free acid, Fe(III), Al(III)	400
Fe(II), Mn(II)	416.7
Sulphate (mg/L)	2933.30
Magnesium (mg/L Mg)	140
Cobalt (mg/L Co)	2.7
Nickel (mg/L Ni)	6
Calcium (mg/L Ca)	518
B. Pre-treatment for metal removal	
Chemicals for pre-treatment	
$Ca(OH)_2$(from Ba stage) (mg/L)	604.3
O_2(mg/L)	59.7
Flow (ML/d)	75
Sodium (mg/L)	45
Chloride (mg/L)	47.3
Sulphate (mg/L)	2650.00
Magnesium (mg/L Mg)	140