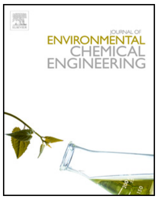
Journal of Environmental Chemical Engineering xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece



Research paper

Direct elemental sulphur recovery from gold acid mine drainage streams

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ARTICLE INFO

Article history:
Received 27 June 2016
Received in revised form 24 October 2016
Accepted 1 November 2016
Available online xxx

Keywords:
Sulphur
Acid mine drainage
Barium carbonate
Barite
Gypsum
Solid waste sludge
Sulphate reduction
Sulphide
Thermal reduction
Stripping

ABSTRACT

The metal precipitates resulting from the neutralization and desalination processes of acid mine water with lime, limestone and barium carbonate are wastes identified as sludge. The composition of these sludges generally comprises hydrated manganese, magnesium hydroxides, gypsum and large amount of barite. Legislation requires that these sludges be disposed in an environmentally acceptable manner to prevent metals from leaching and entering the environment. However; the enormous volumes of sludge produced and the limited disposal spaces present major environmental and economic concerns for the development of a viable technology for acid mine water treatment. This paper assesses the conversion of $CaSO_4/Mg(OH)_2$ and $BaSO_4/CaCO_3$ generated in the water stage of the Alkali Barium Calcium desalination process into sulphur. Africa is a major importer of large tonnages of sulphur at high cost often inflated by the cost of transportation whilst sulphur itself remains a relatively cheap product. This paper investigates a) the reduction of $BaSO_4/CaCO_3$ and $CaSO_4/Mg(OH)_2$ sludges to barium and calcium sulphide; b) the stripping of the sulphide with CO_2 gas and the production of sulphur. Thermal reduction study shows that $BaSO_4/CaCO_3$ and $CaSO_4/Mg(OH)_2$ sludges can be reduced to BaS/CaS with duff carbon in a muffle furnace operating at about 1100 °C with BaS/CaS yield between 70 and 76%. The BaS/CaS formed was slurried in water and CO_2 was used for the stripping of sulphide to form H_2S gas and $BaCO_3/CaCO_3$ precipitate. The H_2S generated was reacted with ferric sulphate to form elemental sulphur. Sulphur with purity between 95.2% and 99.1% was recovered from the sulphate rich wastes.

1. Introduction

The Acid mine drainage (AMD) is a persistent environmental problem at many active and abandoned gold and coal mine sites. The main characteristics of AMD are low pH and high concentrations of dissolved heavy metals and sulphates [1–4]. In order to avoid major environmental impacts, water contaminated by AMD must be treated to remove the metal and the salinity concentrations and increase the pH, before discharging it to the environment [5–10]. The acidity generated needs to be offset by the presence of alkalinity, present as HCO_3^- from the dissolution of basic minerals such as calcium carbonate or biological activity (such as sulphate reduction). Several processes have been applied to prevent the generation of AMD and to treat, control and mitigate its effects as mine waters can contain significant concentrations of sulphuric acid and metal sulphate due to the oxidation of pyritic material in ore bodies and effluents from the uranium leaching process [11]. The acidity of the water is usually neutralized, but the sulphate content of the water is often in contravention of effluent standards. It is estimated that in South Africa, 200 ML/d of mining effluent, saturated with calcium sulphate, is discharged into the public streams of the Pretoria- Witwatersrand-Vereeniging region [11]. This represents a sulphate load of 73 000 t/a. The closure of gold mines on the Witwatersrand has been identified as a threat to the environment due to AMD seepage from flooded underground mine workings, especially the potential impact on the ground water environment. Seepage of contaminated leachate from tailings piles or dams can also be a significant cause of surface and ground water pollution. The search for sulphate removal technologies from sulphate rich wastes has led to the development of the alkali barium calcium (ABC) process for the treatment of sulphate rich wastewater. In this process, $BaCO_3$ is effectively used

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http://dx.doi.org/10.1016/j.jece.2016.11.002
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Please cite this article in press as: J. Mulopo, Direct elemental sulphur recovery from gold acid mine drainage streams, J. Environ. Chem. Eng. (2016), http://dx.doi.org/10.1016/j.jece.2016.11.002

for the removal of sulphates from sulphate rich industrial waste waters via precipitation of barite, and have exhibited a number of advantages over the use of other chemicals [11–13]. The precipitation of barite is favoured due to the low solubility of barite in water (0.0015 g/L). However, the use of $BaCO_3$ in mine water treatment for sulphate removal results in the production of large amounts of barite and gypsum sludge. Besides its numerous existing uses, barite and gypsum can also be thermally processed back to barium sulphide, which then can be used as a starting material for the production of sulphur, thereby increasing the viability of the overall process and reduce environmental pollution. This novel process consists of the following stages:

- Pre-treatment using $CaCO_3$, or lime, for neutralization of the free acid and precipitation of iron(III) and aluminium(III), and CaS for precipitation of the heavy metals as sulphides [13]:

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + CO_2 + H_2O \quad (1)$$

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O \quad (2)$$

$$2\,M^{3+} + 3CaCO_3 + 3H_2O \rightarrow 2M(OH)_3 + 3CO_2 + 3Ca^{2+}\ (M = Fe^{3+},\ Al) \quad (3)$$

- Lime treatment for magnesium removal and partial sulphate removal through gypsum crystallization [13]:

$$Mg^{2+} + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca^{2+} \quad (5)$$

$$Ca^{2+} + {SO_4}^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \quad (6)$$

- pH adjustment [13]:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O\ (7)$$

Removal of sulphate as $BaSO_4$ [13]:

$$Ca^{2+} + {SO_4}^{2-} + BaCO_3 \rightarrow BaSO_4(s) + CaCO_3(s) \quad (8)$$

- Processing of the $CaSO_4.2H_2O/Mg(OH)_2$ sludge to recover CaS and $CaCO_3$ [13]:

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2 \quad (9)$$

- Processing of CaS to produce $Ca(HS)_2$, $CaCO_3$ and H_2S [13]:

$$2CaS + CO_2 + H_2O \rightarrow Ca(HS)_2 + CaCO_3 \quad (10)$$

$$Ca(HS)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2S \quad (11)$$

- Processing of the $BaSO_4/CaCO_3$ sludge to recover BaS and CaO (dewatering and thermal processes) [13]:

$$BaSO_4 + 2C \rightarrow BaS + 2CO_2 \quad (12)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad (13)$$

- Processing of BaS to produce H_2S and barium carbonate [13]:

$$BaS + CO_2 + H_2O \rightarrow BaCO_3 + H_2S \quad (14)$$

The aim of this paper is to assess the potential of sulphur recovery from sulphate rich solid wastes generated during treatment of AMD and in particular the thermal decomposition of the gypsum and barite/calcite sludge to calcium sulphide and barium sulphide respectively, 2) the stripping of the H_2S from barium sulphide and calcium sulphide slurry with CO_2 to form H_2S and 3) the sulphur production using aqueous ferric sulphate solution as absorption medium where H_2S is absorbed and oxidized to elemental sulphur and at the same time, Fe^{3+} is reduced to Fe^{2+}. Elemental sulphur can be removed from the solution and the reactant Fe^{3+} may be regenerated from Fe^{2+} solution by biological oxidation in an aerated bioreactor using Thiobacillus ferrooxidans. One of the most established methods of recovery of elemental sulphur from sulphate rich sludges remains the thermal process which generally requires a heating stage and a reducing agent i.e. coal, activated carbon, natural gas, carbon monoxide or hydroxide. The sulphide rich mineral produced in the

Table 1
Chemical composition of feed and treated water after various water stages.

Parameter	Quality					
	Feed	$CaCO_3$ neutralization (Stage 1)	CaS dosage (Stage 2)	Lime dosage (Stage 3)	CO_2 dosage (Stage 4)	$BaCO_3$ addition (stage 5)
pH	3.3	5.9	6.8	10.9	8.4	8.5
Sulphate (mg/L)	3941	3710	3500	1800	1810	59
Chloride (mg/L)	37	37	37	37	37	37
Alkalinity (mg/L $CaCO_3$)	0			300	60	65
Acidity (mg/L $CaCO_3$)	800	100	50			
Sodium (mg/L)	50	50	50	50	50	50
Magnesium (mg/L)	147	148	146	10	10	10
Calcium (mg/L)	613	920	1580	1040	948	10
Barium (mg/L)						40
Manganese (mg/L)	46.1	46.1	3.8	1.0		
Iron(II) (mg/L)	949	949	11	0.01		
Iron(III) (mg/L)	35	0	0	0		
Aluminium(III) (mg/L)	26.4	0.5				
Cobalt (mg/L)	5	5	0.06			
Nickel (mg/L)	18.00	18.00	0.14			
Zinc (mg/L)	11.90	11.90	0.15			
TDS (mg/L)	6592	5993	5378	2660	2399	265

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