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Metals and sulphate removal from acid mine drainage in two steps via ferrite sludge and barium sulphate formation

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ABSTRACT

In this work, primary test of ferrite formation by coprecipitation method from pure $Fe(NO_3)_3{\cdot}9H_2O$ and $FeSO_4{\cdot}7H_2O$ were evaluated at different pH and temperature by continues stirring using magnetic stirrer. The optimized method was applied on simulated and real acid mine drainage (AMD). The impact of simultaneous removal of metals and sulphate on the magnetic moment of ferrite sludge and addition of ferrite or ferrite sludge seeds into real AMD samples were also investigated. The XRD results of synthesised ferrite from pure binary salts confirmed that presence of heat and increased pH improved the degree of crystallite of ferrite. During neutralization of AMD using sodium hydroxide, gypsum was not precipitated in the absence of calcium hydroxide or barium ions. Consequently, the two step processes were applied; whereby metals are removed in the first step via ferrite sludge formation using sodium hydroxide and followed by treatment of the filtrate with barium chloride or barium hydroxide for complete sulphate removal as barium sulphate precipitate. From the analysis results, the ferrite sludge produced separately from sulphate showed higher magnetic moments than produced simultaneously. In the pH range of 7–8.5, at temperature of 60 °C, 93%, 12%, and 28%, and 99.6%, 57.5% and 47.5% of Fe, Mn and Co were removed from real AMD; in the absence and presence of ferrite seeds in 20 min reaction time, respectively. Furthermore, the rate of metal removals and magnetic moments of synthesised ferrite sludge were increased in the presence of ferrite seeds. Generally, these results indicated that AMD could be used as a resource for production of commercially valuable chemicals, which in turn could help to offset the cost of treatment.

1. Introduction

Due to its environmental consequences, acid mine drainage (AMD) has been recognized as a major challenge to the worldwide mining industry (Kim, 2015; Mckinnon et al., 2000; Moncur et al., 2014). AMD is easily generated by the weathering of sulphide minerals that are exposed to atmospheric conditions during the mining of valuable ores and characterised by high iron(II), sulphate and low toxic trace metals concentration (Sheoran and Sheoran, 2006). AMD is being considered as one of long term water quality issues for mining operations and process plants; particularly, in countries with problem of fresh water supply such as South Africa and Australia (Maree et al., 1989; Geldenhuys et al., 2001; Younger et al., 2002). Formation of AMD is a slow process and also continues to be produced long after the mine closed for centuries or even millennia (Kalin et al., 2006; Logsdon, 2002; Nocete et al., 2005), and the possible reactions which generate AMD are reviewed (Akcil and Koldas, 2006; Kalin et al., 2006; Simate and Ndlovu, 2014). Further, the challenges that faced in tackling the remediation of AMD and means of generating industrial useful chemicals from AMD were addressed well by Simate and Ndlovu (2014). Indeed, there are extensive research reports on the treatment of AMD, economically, among which lime neutralization and precipitation under oxidative conditions are the preferred methods (Maree et al., 2004; Tolonen et al., 2014; Wilmoth and Kennedy, 1979). A major disadvantage of the method are the requirement of large dose of alkaline materials to increase and maintain pH values typically from 4.0 to 6.5 for optimal toxic metal precipitation and removal (McDonald and Grandt, 1981). Furthermore, the sludge has no economic value due to the difficulty of recycling the waste metals (Chen et al., 2014). The waste need to be disposed in landfills that occupy large areas of land,

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which requires special designs to avoid the re-dissolution and subsequent migration of toxic trace metals (McDonald et al., 2006). Therefore, mine sludge requires costly disposal and it can overshadow the operational costs of AMD treatment plant and makes the process unsustainable (Herrera et al., 2007a; Wang et al., 1996). Thus, there is a strong need for a technology that gives sustainability treatment method to AMD. Especially, ferrite processes being suggested as sustainable alternative, mainly because it may be possible to produce an industrially useful chemical out of wastewater (Herrera et al., 2007b). Ferrites are metal oxides with spinel structure, with the general formula of AB_2O_4 ($AO{\cdot}B_2O_3$), where A and B are metallic ions with oxidation state of +2 and +3, respectively. Some of the examples are: $FeAl_2O_4$, $ZnFe_2O_4$, $CuFe_2O_4$, $MnFe_2O_4$, F_3O_4, $NiFe_2O_4$ and $FeCr_2O_4$. Ferrites are useful raw materials as additives to ceramics and paint as pigment (Michalkova et al., 2013; Marcello et al., 2008; Silva et al., 2012), and manufacturing magnetic devices (Tang and Lo, 2013), as adsorbent and catalyst (Flores et al., 2012,). Thus, formation and usage of such ferrites from AMD dramatically decreases the amount of sludge that has to be disposed.

Previous research indicates that possibility of incorporating metal ions into spinel structure of ferrite (Morgan et al., 2005; Yang et al., 2007). In fact, when there are different metallic ions exist in significant concentration in wastewater or particularly in AMD; removal of metals through ferrite sludge formation is not an easy task. Knowledge of influencing factors on ferrite formation such as temperature, pH, presence or absence of ferrite seeds, and open (without lid or exposed to air) or closed (with glass lid or under limited air) conditions are very essential. Research also showed formation of metal hydroxide precipitate as a precondition for ferrite formation; because the interaction of metal hydroxides followed by dehydration results in ferrite formation (Morgan et al., 2005; Wang et al., 1996). Most of those metals commonly found in AMD precipitate below or at about pH 9. For example Fe^{+3} and Al^{+3} (3.5–5), Cu^{+2} (6.5–7.5), Fe^{+2}(7.5–9), Ni^{+2}, Mn^{+2} and Zn^{+2} (8–9.5) pH ranges (Kalin et al., 2006; Singh and Rawat, 1985). Therefore, the objectives of this study were to: (1) determine the lowest possible pH and temperature at which ferrite or ferrite sludge is produced along with high percentage of metal removal from AMD, (2) identify factors that influence magnetic moment of ferrite sludge during simultaneous removal of metals and sulphate using low stoichiometric ratio of barium to sulphate, (3) determine the possibility of ferrite formation and removal of metals such as Fe, Al, Cr, Mn, Co, Ni, Cu and Zn in the presence or absence of ferrite seeds using real AMD, (4) evaluate whether two step process, first removal of metals and second sulphate is feasible for AMD treatment.

2. Materials and methods

For pH adjustment, 1 mol L^{-1} sodium hydroxide prepared from pure sodium hydroxide pellets and standardized by 1 mol L^{-1} hydrochloric acid was used. Under all conditions, the samples were stirred using magnetic stirrer. All chemicals used for preparation of simulated AMD were analytical grade chemicals of purity $\geqslant$98% except $MgSO_4$ which was 96% (Merck, Darmstadt, Germany). Experiments were conducted for 1 h and after which ferrite or ferrite sludge was separated from the solution by filtration using Whatman No 1 filter paper. The precipitate was cleaned three times with deionized water and dried in oven at 105 °C for 6 h. Metal concentration in the filtrate was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES). For calibration, individual pure standards containing 1000 mg L^{-1} of metals in 0.5 mol L^{-1} nitric acid (Ca, Mg, Ba, Al, Mn, Fe, Co, Ni, Cu, and Zn), purchased from C.C IMELMANN (Pty) Ltd., South Africa was used. The schematic diagram of the process is as shown in Fig. Sup. 1 and specific experimental details are given below under each section.

2.1. Ferrite formation test and temperature selection

Analytical grade chemicals containing 0.04 mol $Fe(NO_3)_3{\cdot}9H_2O$ and 0.02 mol $FeSO_4{\cdot}7H_2O$ dissolved in 500 mL deionized water were used for the preliminary test of ferrite formation. Effects of pH and temperature were also studied by adjusting pH to 4.5, 8.5 and 11.5, and temperature at 25, 40, 60 and 75 °C. The reaction was stopped after stirring for 1 h, and the samples filtered, precipitate cleaned and dried. Finally, the dried samples magnetic moment were determined and characterized.

2.2. Preparation of simulated AMD and treatment procedure

Simulated AMD was prepared from salts of $CaCl_2$, $BaCl_2{\cdot}2H_2O$, $CuSO_4{\cdot}5H_2O$, $MgCl_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $FeSO_4{\cdot}7H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $MnSO_4{\cdot}H_2O$, $ZnCl_2$ and $Ni(NO_3)_2{\cdot}6H_2O$. Salts were weighed to achieve a desired 2:1 mol ratio of trivalent to bivalent ions present in the spinel structure of ferrite. Accordingly, the aforementioned salts containing 5.09, 18, 1.2 and 0.75 mmol (millimole) of Fe^{2+}, Fe^{+3}, Al^{+3} and M^{+2} (Mg^{+2}, Cu^{+2}, Co^{+2}, Mn^{+2} and Zn^{+2}), respectively were dissolved in ultrapure Milli-Q water having a conductivity of 0.055 μS cm^{-1} in 250 mL volumetric flask. In addition, despite their well-documented influences in ferrite formation, each salt containing 1.46 mmol of Ba^{+2} and Ca^{+2} ions were added to observe their impact in sulphate removal. Since these ions preferentially form sulphate precipitate than entering into spinel structure of ferrite, their concentrations were not included into the calculation of moles of divalent (Wang et al., 1996). It should be noted that metal composition of AMD varies widely from site to site (Sheoran and Sheoran, 2006). In this study, approximate average metal concentrations detected in different sites of AMD in South Africa were used.

The blanks containing ultrapure Milli-Q water and sodium hydroxide also run under similar condition. During sampling time, the surface of magnetic stirrer was well observed to confirm the presence or absence of any adhered magnetic particles. Regularly, 10 mL samples were taken at 0, 10, 20, 40 and 60 min and then filtered, concentration of corresponding metals and sulphate contents were determined.

2.3. Leaching test of ferrite sludge

The stability of produced ferrite sludge was evaluated by leaching test taking 0.5 g of dry ferrite sludge obtained at an average pH of 11.9 and 8.4 (open). The leaching processes were conducted at an average pH of 5.5 and 6.6, respectively. The samples were added into 100 mL beaker and 80 mL of ultrapure Milli-Q water was added, and acidified by drop wise addition of 1 mol L^{-1} nitric acid until the pH of the solution less than 7 was attained. Thereafter, the solution stirred for 1 h, filtered and then concentration of leached metals in the filtrate was determined. The residue sample of each experiment was cleaned by deionized water; dried and the corresponding magnetic moment was determined.

2.4. Preparation of simulated AMD for Sulphate removal test

For the sulphate removal test, synthetic AMD water was prepared by dissolving soluble salts each containing 3.64 mmol of sulphate ($CuSO_4{\cdot}5H_2O$, $MgSO_4{\cdot}H_2O$, $FeSO_4{\cdot}7H_2O$, $MnSO_4{\cdot}H_2O$, $ZnSO_4{\cdot}7H_2O$, $NiSO_4{\cdot}6H_2O$), $Co(NO_3)_2$, $Ca(OH)_2$, and $BaCl_2{\cdot}2H_2O$. Calculated amount of salts containing trivalent ions $Al(NO_3)_3$ and