

Fe(II) oxidation during acid mine drainage neutralization in a pilot scale sequencing batch reactor

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ABSTRACT

This study investigated Fe(II) oxidation during acid mine drainage (AMD) neutralization using CaCO₃ in a pilot scale Sequencing Batch Reactor (SBR) of hydraulic retention time (HRT) of 90 min and sludge retention time (SRT) of 360 min in the presence of air. The removal kinetics of Fe(II), of initial concentration 1033 ± 0 mg/L, from AMD through oxidation to Fe(III) was observed to depend on both pH and suspended solids, resulting in Fe(II) levels of 679 ± 32 mg/L, 242 ± 64 mg/L, 46 ± 16 mg/L and 28 ± 0 mg/L recorded after cycles 1, 2, 3 and 4 respectively, with complete Fe(II) oxidation only achieved after complete neutralization of AMD. Generally, it takes 30 min to completely oxidize Fe(II) during cycle 4, suggesting that further optimization of SBR operation based on both pH and suspended solids manipulation can result in significant reduction of the number cycles required to achieve acceptable Fe(II) oxidation for removal as ferric hydroxide. Overall, complete removal of Fe(II) during AMD neutralization is attractive as it promotes recovery of better quality waste gypsum, key to downstream gypsum beneficiation for recovery of valuables, thereby enabling some treatment cost recovery and prevention of environmental pollution from dumping of sludge into landfills.

Keywords: Acid Mine Drainage, Fe(II) oxidation, Sequencing Batch Reactor

INTRODUCTION

Globally, acid mine drainage (AMD) has already been identified as a major environmental problem facing the mineral industry (Ribet et al. 1995) resulting in serious and sometimes permanent ecological damage (Micera & Dessi 1988). The detrimental effect of AMD on the environment has been widely studied and reported (Baird 1995; Bell et al. 2002). On the other hand, a wide range of AMD treatment technologies has been developed and globally proven with a number of research articles and reviews providing quantitative data in terms of energy consumption, cost, and ease of application and technological trends available (Ackman & Kleinmann 1991; Akcil & Koldas 2006; Egiebor & Oni 2007; Zhuang 2009).

Johannesburg is a hub of gold mining in South Africa and the rest of the world, sprawling across a topographical upland known as the Witwatersrand, divided into east, west, far west and central rand basins. Over the past century the Witwatersrand gold bearing reef has yielded 40% of all the gold ever mined on earth (Hanlon, 2010). This extensive mining has significantly altered the groundwater hydrology of the basin resulting in generation of low pH water rich in iron(II), sulphate and heavy metals, generally known as AMD. In 2002, AMD from the lowest lying mine shafts in west rand basin started decanting at a rate of 15 to 35 ML/day (Coetzee et al. 2004) posing threats to the Krugersdorp Game Reserve and the Cradle of Humankind World Heritage Site. Although a reclamation plant was established to treat the decanting AMD; multiple deficiencies were identified, including failure of remediation approach to capture all decanting point sources, resulting in untreated AMD entering the watershed (Hanlon 2010).

A report (Coetzee et al. 2010) prepared by a team of experts appointed by the South African Government-appointed Inter-Ministerial Committee on AMD recommended construction of a 20 ML/d emergency neutralization plant as one of the short-term interventions to deal with uncontrolled AMD decanting from the Witwatersrand's Western Basin. Treatment of AMD using CaCO_3 and Ca(OH)_2 is a widely used approach in South Africa (Vadapalli et al 2008). Moreover, the CSIR has developed an integrated $\text{CaCO}_3/\text{Ca(OH)}_2$ neutralization process capable of reducing sulphate concentration in AMD to about 1,200 mg/L (Geldenhuys et al. 2003), with several full-scale plants operational worldwide. Based on this background, the Trans-Caledon Tunnel Authority, an implementation agency for the South African Department of Water Affairs is currently implementing the short term intervention plan. However this short term interventions plan, although necessary at this stage, is not integrative enough to include opportunities for sludge beneficiation as a strategy to recover some costs associated with AMD neutralization. With opportunities for waste gypsum beneficiation and application having been recently reported (Zvimba et al. 2011; Zvimba et al. 2012), there is significant need to ensure the short term interventions plan is configured to allow subsequent beneficiation of sludge in order to provide a sustainable AMD solution.

A Sequencing Batch Reactor (SBR) is designed to operate in batch mode under non-steady state conditions with sludge settlement occurring in the same tank producing sludge of good settling properties. Using limestone as neutralizing agent 4 g/L iron(II) have been reportedly oxidized within 2 hr in sequential batch mode while 5 hr were required under continuous conditions (Maree et al., 2004). The use of SBR also alleviates challenges of pumping slurries at low flows representative of full scale plant. In this regard, the current study investigated iron(II) oxidation kinetics during AMD neutralization using CaCO_3 in a pilot scale SBR and also assessed the effect of pH and suspended solids. Overall, a clear understanding of iron(II) oxidation during AMD neutralization will provide insights into our

ability to effectively remove ferrous iron from AMD and separate it from waste gypsum sludge for subsequent beneficiation.

MATERIALS AND METHODS

Feedstock

AMD containing about 1033 mg/L Fe (II), 3000–4000 mg/L SO_4^{2-} , pH ranging 5.0–5.5 and acidity of about 2000 mg/L CaCO_3 equivalent was collected from the Western Basin of the Witwatersrand basin and used as feed water. Commercial CaCO_3 (98% purity) purchased from Associated Chemical Enterprise (ACE) was used as the neutralization agent.

Equipment

AMD neutralization was carried out batch wise using SBR 1 with reactor 2 used for collecting neutralized AMD as given in Figure 1. SBR 1 was operated on a four stage cycle sequence namely; fill (5 min), reaction (30 min), settling (60 min), and decant stage (5min). A Hanna HI 2829 multi-parameter data logger was used to continuously record SBR 1 pH, while a Toledo Auto-titrator was used for acidity determination. A HaCH DR/2010 spectrophotometer was used for sulphate determination at 450 nm.

Experimental procedure

The SBR program was used for SBR 1. AMD (~24 L) was pumped into SBR 1 during the fill stage at the start of the cycle and solid CaCO_3 was immediately introduced upon commencing of stirring and aeration. As the neutralization progressed, sample aliquots were collected at specific time points during the reaction stage for the determination of Fe(II), acidity and sulphate. After the reaction stage, the aeration and mixing stopped in accordance to the SBR program and the sludge containing a mixture of $\text{Fe}(\text{OH})_3$, un-dissolved CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was allowed to settle for 60 min. After 60 min of settling, the clarified AMD at a pH of about 5.9 was pumped out of SBR 1 into reactor 2. The whole cycle from fill to decanting of neutralized AMD was then repeated without sludge removal while Fe(II) oxidation was continuously monitored. Four cycles were required to achieve adequate Fe(II) oxidation during AMD neutralization. For one run consisting of four cycles, the hydrodynamic retention time (HRT) and sludge retention time (SRT) for SBR 1 were 1.5 hrs and 6 hrs respectively, and Fe(II) oxidation runs and measurements were carried out in triplicates.

Analytical procedure

AMD quality was determined before neutralization, after neutralization and also after gypsum crystallization for metal content using ICP-OES (Varian: Vista Pro CCD Simultaneous ICP-OES). The pH, acidity and alkalinity of the AMD were determined using a Mettler Toledo Auto-titrator following filtration. Fe(II) was determined by standard permanganate titrimetric technique (APHA et al. 1992) while sulphate was determined using a HaCH DR/2010 spectrophotometer at 450 nm.

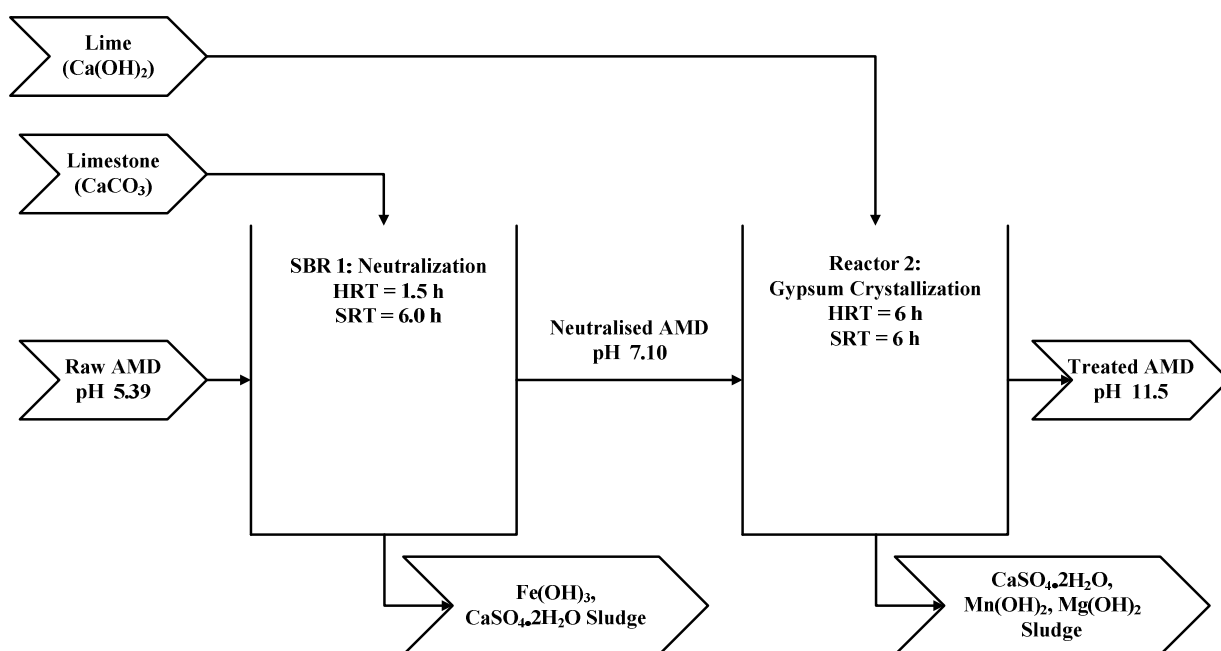


Figure 1 Schematic representation of the SBR pilot plant

RESULTS AND DISCUSSION

AMD Quality

Table 1 shows the quality of the feed AMD, before SBR neutralization, after neutralization and gypsum crystallization. It can be seen from Table 1 that the major AMD parameters include high Fe(II), acidity and sulphate. In this regard, Fe(II) decreased from 1033 ± 0 mg/L to $<29 \pm 0$ mg/L after SBR neutralization, with less than 0.03 ± 0.01 mg/L Fe(II) remaining following addition of Ca(OH)_2 during gypsum crystallization. The acidity decreased from 1773 mg/L CaCO_3 equivalent to 120 after SBR neutralization, with zero acidity remaining following addition of Ca(OH)_2 after gypsum crystallization. The removal of sulphate from AMD containing about 3800 mg/L resulted in sulphate levels of 2500 mg/L while further sulphate removal was achieved to 1368 mg/L upon addition of more soluble Ca(OH)_2 resulting in gypsum crystallization. The removal of metals is a result of formation of metal hydroxides as the pH of the AMD increases upon dissolution of CaCO_3 . The metal hydroxide formation is highly depended on their solubility with different metals removed under different pH conditions. In this regard, the aerial oxidation of Fe(II) to Fe(III) during AMD neutralization in a pilot scale SBR is critical in order to remove Fe(II) as Fe(OH)_3 precipitating under mild acidic conditions (<6.0) as opposed to Fe(OH)_2 which precipitates within pH range 8 – 9 (alkaline conditions), resulting in significant contamination of gypsum useful for downstream recovery of valuables.

Table 1 Feed AMD quality before and after SBR neutralization

Parameter	Before SBR neutralization	After SBR neutralization	After gypsum crystallization	WHO (DWA) limit
pH	5.39	7.10	11.5	6-9
Acidity (mg/L CaCO ₃)	1773	120	0	NA
Fe(II) (mg/L)	1033	<29	<0.025	0-0.3 (0-0.1)
Na (mg/L)	110	107	129	0-200 (0-100)
Mg (mg/L)	180	198	2	0-30
Mn (mg/L)	46	51	<0.025	0-0.1 (0-0.05)
Al (mg/L)	<0.1	<0.1	<0.1	0-0.2 (0-0.15)
Ca (mg/L)	580	953	1102	0-32
Co (mg/L)	0.24	0.41	<0.025	NA
Ni (mg/L)	0.12	0.26	0.085	NA
Zn (mg/L)	0.031	0.046	<0.025	0-3 (0-0.5)
SO ₄ ²⁻ (mg/L)	3800	2500	1368	0-500

Note: values in brackets obtained from Department of Water Affairs (DWA) of South Africa 1996 if the values are different from those indicated by the World Health Organization (WHO), 2011. NA stands for not applicable.

Fe(II) oxidation kinetics - effect of pH and suspended sludge

Figure 2 shows the results obtained for Fe(II) oxidation kinetics when AMD is neutralized in a pilot scale SBR using CaCO₃ in the presence of air. From Figure 2, it can be observed that Fe(II) oxidation kinetics significantly improves from cycle 1 to 4 as final cycle pH increases from 5.4 to 7.1 while the suspended solids increased from 0 to 11.1 g/L in the SBR. In this regard, Fe(II) decreases from 1033 ± 0 mg/L to 679 ± 32 mg/L, 242 ± 64 mg/L, 46 ± 16 mg/L and <29 ± 0 mg/L after cycles 1, 2, 3 and 4 respectively, over a period of 100 min following neutralization using commercial CaCO₃.

The rate of Fe(II) oxidation at different pH ranges using synthetic acidic feed water has been reported by Maree et al. (1999), with biological Fe(II) oxidation favored at pH lower than 5 while chemical Fe(II) oxidation reportedly favored at higher pH. In the pH range 5 – 6, which is of greater importance from the point of view of AMD neutralization using CaCO₃, it has been established that Fe(II) oxidation highly depends on Fe(II), O₂, OH⁻, CaCO₃, reactor surface area and suspended solids concentration. Based on the data given in Table 1, where the AMD pH changed from 5.4 to 7.1 during AMD neutralization using CaCO₃, one would expect both biological and chemical Fe(II) oxidation to occur provided appropriate support system for microorganisms is available. However, the absence of such appropriate support medium in our pilot scale plant configuration obviously limited biological Fe(II) oxidation, and therefore chemical Fe(II) oxidation has been considered predominant. Generally, neutralization of AMD using CaCO₃ normally results in pH ranging between 6 and 7 because of CO₂ buffering during CaCO₃ dissolution. However, AMD neutralization in which AMD pH as high as 8.0 was achieved has been reported (Zvimba et al. 2012), and as such a final AMD neutralization pH slightly above 7 reported in this study is therefore not surprising.

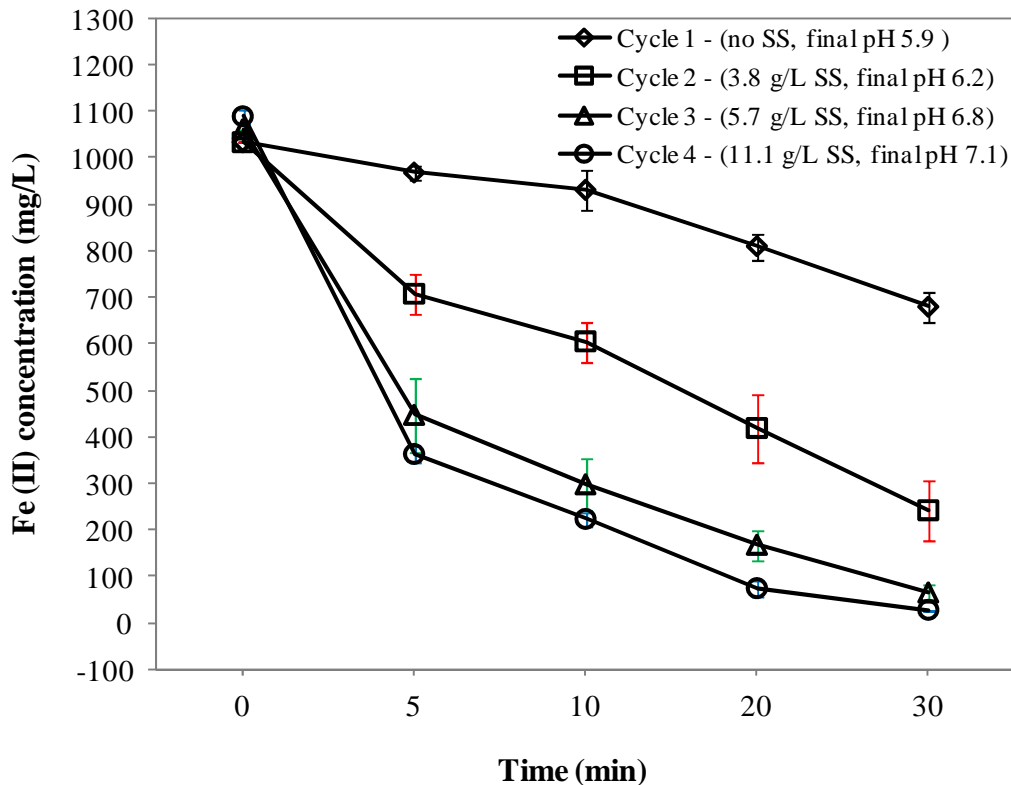
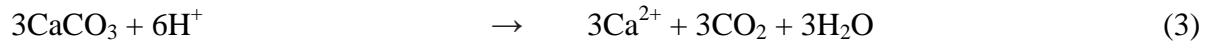


Figure 2 Fe(II) oxidation kinetics over four cycles during pilot scale AMD neutralization in a SBR.

It is worth noting that the rate of Fe(II) oxidation during AMD neutralization over the 4 cycles improved significantly with increased suspended solids, of which 3.8, 5.8 and 11.1g/l of suspended solids were measured before cycles 2, 3 and 4 respectively. Suspended solids have been reported as one of the critical parameters influencing Fe(II) oxidation within pH range 5 – 6 (Maree et al. (1999)). In fact suspended solids and Fe(II) concentration are likely to impact on Fe(II) oxidation kinetics during pilot scale AMD neutralization in a SBR since all the other parameters (O_2 , $CaCO_3$, reactor surface area) were generally fixed in the SBR. This therefore provides an opportunity to optimize the SBR based on pH and suspended solid content manipulation, therefore using this to achieve the best Fe(II) oxidation as shown in Figure 2. Although $CaCO_3$ particles are generally considered to be coated with a ferric hydroxide layer during neutralization, which may prevent further dissolution of $CaCO_3$, at Fe(II) concentrations greater than 200 mg/L, it appears the suspended solids impacted more positively on Fe(II) oxidation during pilot scale AMD neutralization in a SBR, a phenomenon ascribed to generation of acidity by hydrolysis of Fe(II) as shown in equation 2.

Figure 3 shows the chemical behavior of the most critical AMD parameters, after dosing AMD with $CaCO_3$ in a pilot scale SBR for cycle 4. From Figure 3, the complete neutralization of Fe(II)-rich AMD was only achieved after completion of Fe(II) oxidation (Reaction 1). This is attributed to the acidity generation resulting from hydrolysis of Fe(III) (Reaction 2) that would require further neutralization by $CaCO_3$ (Reaction 3), and as such promotes further $CaCO_3$ dissolution with AMD pH increasing to above 6.8 following complete Fe(II) oxidation.



Overall, equations 4 and 5 denote what happens in SBR 1 (AMD neutralization) and reactor 2 (gypsum crystallization), respectively.



M represents either Magnesium or Manganese.

Based on equations 1 and 4, the removal of Fe(II) as ferric hydroxide during AMD neutralization is desirable as it promotes generation of less contaminated waste gypsum as given in equation 5 for subsequent downstream beneficiation.

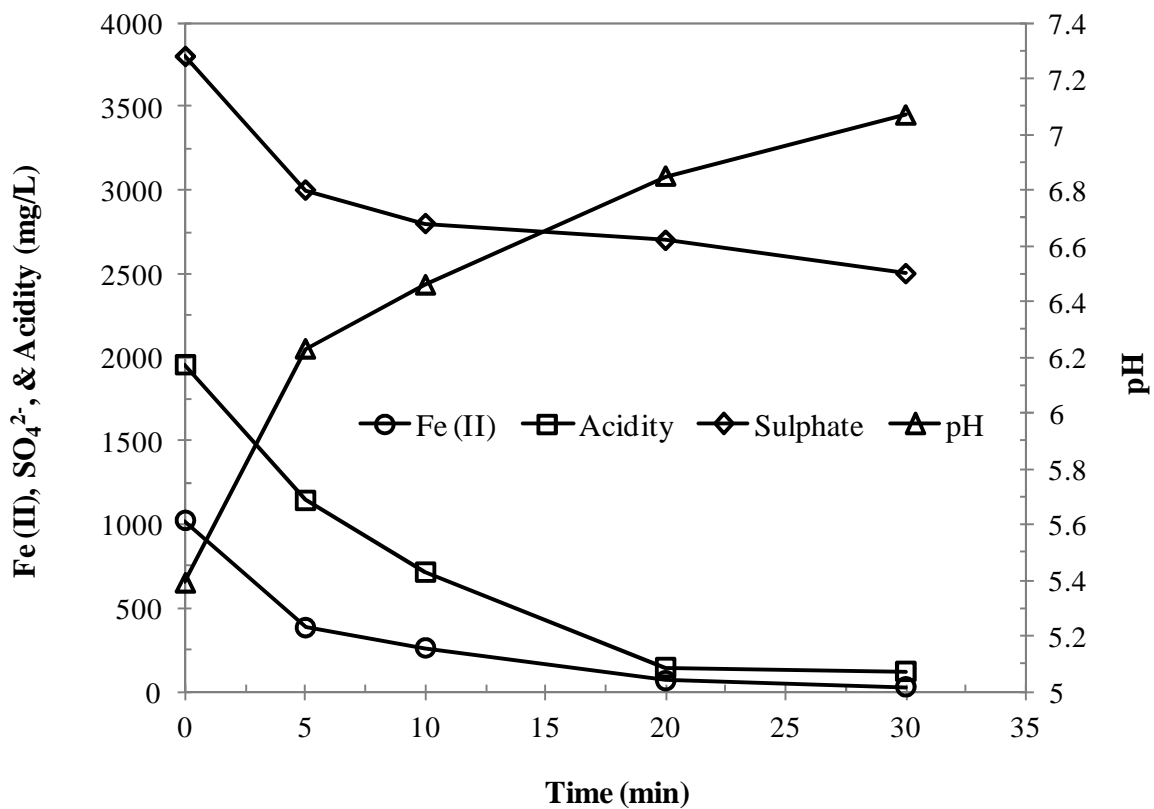


Figure 3 Temporal removal of Fe(II), acidity, and sulphate during AMD neutralization in a pilot scale SBR.

However, sulphate could only be decreased from 3800 to 2500 mg/L during pilot scale AMD neutralization using CaCO_3 , with further sulphate removal to 1368 mg/L achieved after adding more soluble $\text{Ca}(\text{OH})_2$ as shown in Table 1. This suggested the impact of gypsum solubility ranging 2.0 - 2.5 g/L on sulphate removal. Generally, from Figure 3, it takes about

30 minutes to completely oxidize Fe(II), remove acidity and reduce sulphate to about 2.5 g/L in a pilot scale SBR during cycle 4, suggesting that AMD Fe(II) oxidation during CaCO₃ neutralization in a SBR can be further optimized resulting in reduction of number of cycles required to achieve acceptable AMD quality. In a related study, Maree et al. (1999) has reported complete oxidation of Fe(II) in more than 1 hr using synthetic acidic feed water. It appears large quantities of suspended solids associated with the pilot scale SBR, particularly for cycle 4 (11.1 g/L) also plays significant role in improving the Fe(II) oxidation kinetics. Moreover, the use of CaCO₃ for neutralization becomes more beneficial if rapid Fe(II) oxidation is attainable. In this regard, the use of CaCO₃ as a neutralization agent has been reported to oxidize 4000 mg/L Fe(II) within 2 hr when operating the plant in sequential batch mode and within 5 hr under continuous conditions (Maree et al., 2004), with a clarifier required to return sludge to the neutralization reactor to maintain a minimum concentration of suspended solids. The essence of this minimum suspended solid has also been demonstrated in our study as given in Figure 2 where suspended solids clearly impacted on Fe(II) oxidation. It is also worth noting that the settling characteristics of the suspended solids generated during AMD neutralization in a pilot scale SBR were quite similar for all cycles and these could easily settle and separate from the neutralized AMD.

CONCLUSIONS

Based on the current study, Fe(II) oxidation during AMD neutralization in a pilot scale SBR was achieved over 4 cycles. In this regard, the Fe(II) oxidation kinetics in the SBR were observed to depend on pH and suspended solids, with AMD containing 1033 ± 0 mg/L Fe(II) oxidized to 679 ± 32 mg/L (cycle 1, AMD final pH 5.4), 242 ± 64 mg/L (cycle 2, AMD final pH 6.2), 46 ± 16 mg/L (cycle 3, AMD final pH 6.8) and $<28 \pm 0$ mg/L (cycle 4, AMD final pH 7.1) as the initial suspended solid content in the SBR changed from 0, 3.8, 5.7 to 11.1 g/L respectively. The fact that most parameters (O₂, CaCO₃, reactor surface area) that also influence Fe(II) oxidation kinetics were generally fixed in the SBR configuration, and as such would not be expected to impact significantly on Fe(II) oxidation rate suggesting that changes in pH and suspended solid content in the SBR are the most critical parameters that may be useful for Fe(II) oxidation optimization for large scale AMD neutralization. Generally, it takes 30 min to completely oxidize Fe(II) in a pilot scale SBR (cycle 4), and with further optimization of SBR operation the number of cycles required to achieve acceptable Fe(II) oxidation can be reduced. Overall the study promotes further understanding as we aspire to achieve complete removal of Fe(II) from AMD during neutralization using CaCO₃ so as to ensure generation of better quality waste gypsum for downstream beneficiation, thereby significantly preventing environmental pollution through dumping of waste sludge into landfills.

Acknowledgements

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