Removal of sulphates from South African mine water using coal fly ash

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Abstract South African power stations generate large amounts of highly alkaline fly ash (FA) which has a serious impact on the environment. Acid mine drainage (AMD) is another environmental problem containing high concentration of heavy metal and SO_4^{2-}. Several studies have shown that 80—90 % of SO_4^{2-} can be removed when FA is co-disposed with AMD rich in Fe and Al. Many sources of contaminated mine waters in South Africa have circumneutral pH and much lower concentrations of Fe and Al, but are rich in Ca, Mg and SO_4^{2-}. This study evaluated SO_4^{2-} removal from neutral mine drainage (NMD) and AMD using FA.

Key Words sulphates, acid mine drainage, neutral mine drainage, fly ash, ettringite

Introduction

Mine water is a source of heavy metal and sulphate contamination of surface and groundwater. Due to the high costs associated with chemical treatment technologies and long residence time requirement for biological treatment, there has been concerted effort toward developing a cost effective technology for treatment of mine water. The treatment of mine water using coal FA has proved to be promising (Petrik et al., 2003; Gitari et al., 2006 and Gitari et al., 2008).

Recently, it was shown that treatment of NMD rich in Mg and Ca to pH 9 with FA did not result in a significant sulphate removal (Madzivire et al., 2008). The objective of this study was to attempt to provide an understanding by the use PHREEQC geochemical modelling tool to investigate the effect of Fe and Al on sulphate removal from NMD when reacted with FA. The Al and Fe were added by mixing AMD with NMD. This study would also provide the understanding of the mineral phases responsible for removal of sulphates, Fe, Al and Mn from mine water.

Method

The mine waters, NMD and AMD were collected from two different coal mines in Mpumalanga, South Africa. The mine water was filtered and analysed by inductively-coupled plasma-atomic emission/mass spectrometry (ICP-AES/MS) and ion chromatography (IC) for cations and anions, respectively. The FA was collected directly from the precipitators, from a nearby pulverized coal combustion power station in Mpumalanga, and kept in sealed plastic bags devoid of air to avoid carbonation of free lime to calcite.

NMD and AMD were mixed in the following ratios; 1:0, 1:1, 2:1 and 3:1 (NMD:AMD). AMD was used as a source of Fe and Al. The 1:0 ratio had a pH of 6.5 and therefore it is NMD while 1:1, 2:1 and 3:1 mixtures had pH values less than 3 representing different AMD types. These AMD types varied in the amount of Fe, Al and sulphates depending on the AMD added. Mixtures were then treated with FA at a liquid/solid ratio of 2:1 by stirring with an overhead stirrer (Madzivire et al., 2008). Aliquot samples were collected at pH 6, 8, 9, 10, 11 and 12, filtered and then analysed. The mineral phases that formed were elucidated by X-ray diffraction spectroscopy (XRD). The mineral phases that were likely to form at various pH levels were predicted by PHREEQC geochemical modelling and WATEQ4F database (Parkhurst and Appelo, 1999). The WATEQ4F database was edited to include the thermodynamic parameters of ettringite as calculated by Perkins and Palmer (1999).

Results and discussion

Results reveal that the amount of sulphates, Mg, Mn, Al and Fe removed from the NMD and NMD/AMD mixtures depends on the final pH of the water (Fig 1a-e). Also Figure 1f shows that the amount of Ca increases with increase in the final pH.

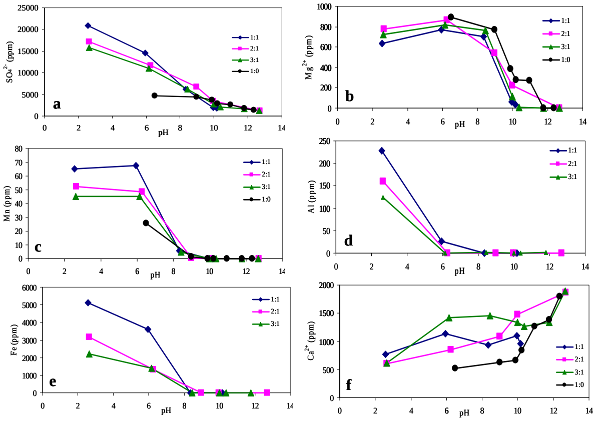

Figure 1 *Concentration of sulphate (a), Mg (b), Mn (c), Al(d), Fe (e), Ca (f) during treatment of NMD and AMD with FA to various pH values*

Possible sulphates mineral phases that were precipitating at different pH levels were predicted using PHREEQC geochemical model and the results are shown in Figure 2.

Saturation indices (SI) of different sulphate mineral phases for NMD/FA mixtures at different pH values (Fig 2a) show that gypsum, barite, celestite, anhydrite and ettringite are the only mineral phases that could precipitate out sulphate when NMD was mixed with FA. The amount of sulphate that could be removed as ettringite, barite and celestite were insignificant since the concentration of Al, Ba, and Sr were very low in NMD meaning that gypsum was the main mineral controlling sulphate removal from NMD.

Saturation indices calculated for the AMD (Fig 2b) using PHREEQC model show that, in addition to gypsum, celestite, ettringite and anhydrite, other Fe and Al oxyhydroxysulphates (alunite, basaluminite, jarosite(ss), jarosite-k, jarosite-Na, jarosite-H and jurbanite) contribute to sulphate removal. All the oxyhydroxysulphates are super saturated at pH 4—10 except ettringite. Above pH 10 they become under saturated and ettringite becomes supersaturated. This explains why the AMD mixtures tend to precipitate out more sulphate compared to NMD when pH was raised to below 10 (Fig 1a).

The PHREEQC model was validated by the XRD spectra. The mineral responsible for sulphate removal was analysed by comparing XRD spectra of FA before and after reacting it with NMD and AMD (Fig 3). From the XRD spectrum of solid residues collected after NMD was treated with FA to pH 12.3 the mineral phase that formed was found to be gypsum. On the other hand the mineral phases detected by XRD for solid residues collected after treating AMD with FA were gypsum and ettringite.

PHREEQC geochemical modeling predicts that Mg would start to precipitate at pH 8.5 (Fig 4) as brucite ($Mg(OH)_2$). At pH above 10, $Mg(OH)_2$ is supersaturated, consequently the Mg concentration decreased to below 0.3 ppm due to the formation of $Mg(OH)_2$ correlating well with the results of ICP (Fig 1b).

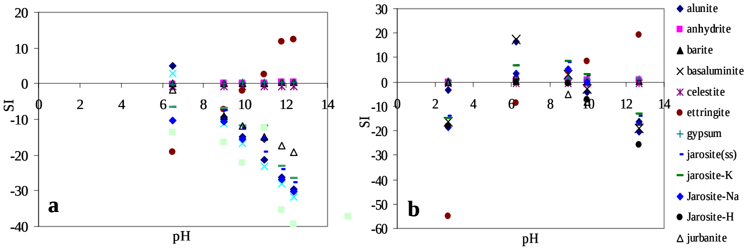

Figure 2 *Saturation indices obtained from PHREEQC model of sulphate minerals of NMD (a) and AMD mixtures (b) at various pH values*

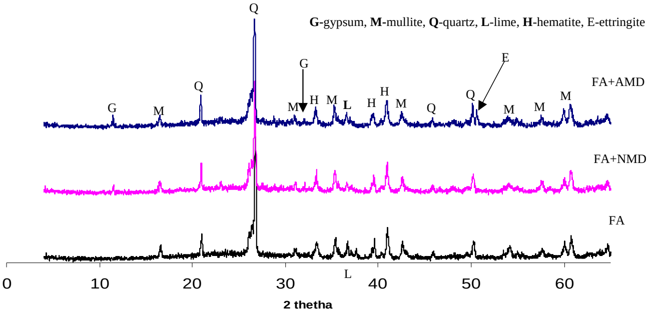

Figure 3 *XRD spectra of FA, solid residues after treatment of NMD with FA to pH 12.34(FA+NMD) and solid residues after treatment of AMD with FA to pH 12.23 (FA+AMD)*

Saturation indices obtained using PHREEQC showed that Mn bearing mineral phases start precipitating at pH greater than 8 (Fig 5) as birnessite (MnO_2), bixbyite (Mn_2O_3), hausmannite (Mn_3O_4), manganite ($MnOOH$), nsutite (MnO_2), pyrochroite ($Mn(OH)_2$) and pyrolusite (MnO_2). All these mineral phases approach saturation at pH 8.5 and are supersaturated at pH greater than 9, and thus precipitate out rapidly and completely.

The SI was calculated for Al and Fe bearing mineral phases using PHREEQC geochemical model (Fig 6). The calculated SI indicated that the Al mineral phases are amorphous $Al(OH)_3$, alunite ($KAl_3(SO_4)(OH)_6$), basaluminite ($Al_4(OH)_{10}SO_4$), boehmite ($AlOOH$), diaspore ($AlOOH$), ettringite, jurbanite ($AlOHSO_4$) and gibbsite ($Al(OH)_3$) could precipitate out when mine water was treated with FA (Fig 6a). Amorphous $Al(OH)_3$, alunite, basaluminite and jurbanite are supersaturated between pH 4—9, while boehmite, diaspore and gibbsite are supersaturated at pH greater than 4. Ettringite is supersaturated at pH greater than 10. Calculated SI showed that Fe hydroxides, oxyhydroxides and oxyhydroxysulphate mineral phases started precipitating at pH 5 (Fig 6b). The minerals controlling Fe removal according to the model are $Fe(OH)_{2.7}Cl_{0.3}$, amorphous $Fe(OH)_3$, $Fe_3(OH)_8$, goethite ($FeOOH$), hematite (Fe_2O_3), maghematite (Fe_2O_3), magenetite (Fe_3O_4), jarosite(ss) ($K_{0.77}Na_{0.03}H_{0.2}Fe_3(SO_4)_2(OH)_6$), jarosite-K ($KFe_3(SO_4)_2(OH)_6$, jarosite-Na ($NaFe_3(SO_4)_2(OH)_6$) and

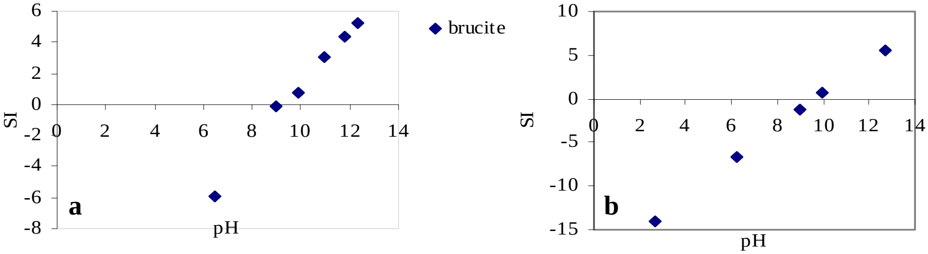

Figure 4 *Saturation indices obtained from PHREEQC model of Mg minerals of NMD (a) and AMD mixtures (b) at various pH values*

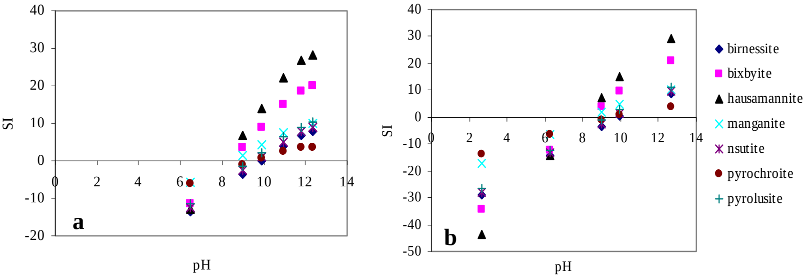

Figure 5 *Saturation indices obtained from PHREEQC model of Mn minerals of NMD (a) and AMD mixtures (b) at various pH values*

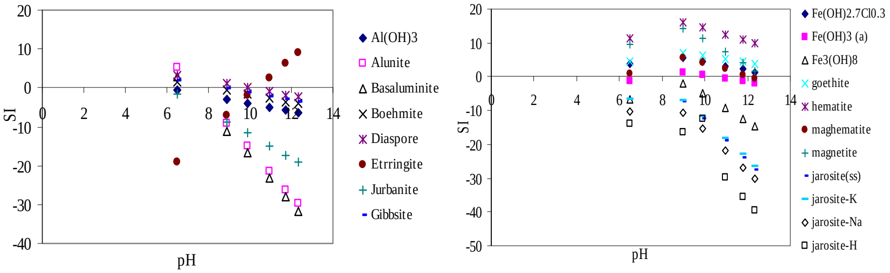

Figure 6 *Saturation indices obtained from PHREEQC model of Al (a) and Fe (b) for AMD mixtures at various pH values*

jarosite-H ($HFe_3(SO_4)_2(OH)_6$). All other Fe bearing mineral phases are capable of precipitating at pH greater than 4 except jarosite-H which is stable at pH 6—7, jarosite-Na is stable at pH 4—9, while jarosite-K and jarosite(ss) are stable between pH 4—10.

Conclusion

Removal of sulphates, Fe, Al, Mg and Mn when NMD and AMD were treated with coal FA was found to be pH dependent. About 16 % of sulphates were removed when NMD was treated with FA to pH 10 and 71 % of sulphates was removed when pH was increased beyond 10. In case of AMD 80 % of sulphates were removed when the pH was raised to 10 and 90 % was removed when pH of AMD was raised to greater 10. Presence of Fe and Al in AMD enhanced sulphate removal through precipitation of Fe and Al oxyhydroxysulphates. If the mine water pH was raised to greater than 6, 8, 9 and 11 it was found that approximately 100 % of Al, Fe, Mn and Mg were removed respectively. The mineral phases that were responsible for sulphate removal were found to be alunite, anhydrite, barite, basaluminite, jurbanite, jarosite-ss, jarosite-K, jarosite-Na, jarosite-H, celestite and gypsum. Iron was found to be precipitating in the form of $Fe(OH)_{2.7}Cl_{0.3}$, amorphous $Fe(OH)_3$, $Fe_3(OH)_8$, goethite, hematite, maghematite, magenetite, jarosite(ss), jarosite-K, jarosite-Na and jarosite-H, while Al was found to be precipitating out as amorphous $Al(OH)_3$, alunite, basaluminite, boehmite, diaspore, ettringite, jurbanite and gibbsite. Mg was found to be removed as brucite and Mn was found to be removed as birnessite, bixbyite, hausamannite, manganite, nsutite, pyrochroite and pyrolusite.

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