

Efficacies of Pervious Concrete and Zero-Valent Iron as Reactive Media for Treating Acid Mine Drainage

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Abstract

Batch reactor tests using pervious concrete (PervC) made at 0.27 water/cement ratio by mixing granite aggregate and Portland cement CEM I 52.5 R were performed to compare the use of PervC versus zero-valent iron (ZVI) for treatment of Acid Mine Drainage (AMD). The removal rates for Ca, Mg, Al, Fe, Mn, SO₄ and Cu were greater for AMD samples that were treated with PervC reactive media relative to those treated with ZVI. The pH-driven metal precipitation and adsorption of precipitates onto the surface of PervC and gypsum by-product are the main mechanisms of removal of metals from AMD.

Keywords: removal mechanisms, pervious concrete, acid mine drainage, batch reactor test, zero-valent iron

Introduction

Recent researches have shown pervious concrete to be a promising reactive material for effectively treating acid mine drainage (AMD) using the permeable reactive barrier (PRB) system. Pervious concrete is made by mixing a single-size coarse aggregate with cement to form a binder matrix of a highly porous network. During AMD treatment, the polluted water is percolated through pervious concrete at a sufficiently low controlled rate, to allow chemical interaction between the AMD and concrete. It has been shown that pervious concrete may be a more effective adsorbent than most other established reactive materials used in PRBs for treating AMD, such as zero-valent iron (ZVI) and zeolites (Ekolu and Bitandi 2018; Shabalala and Ekolu 2019; Solpuker et al. 2014; Majersky 2009).

The reactions resulting from the treatment of AMD using pervious concrete PRB, leads to an increase in the pH of AMD, causing most metals including Al, Zn, Fe, Cu, and Pb present in the polluted water to precipitate out of solution in form of metal hydroxides (Seneviratne 2007). Furthermore, the dissolved sulfate in the AMD react with Ca(OH)₂ in concrete to form gypsum. The formation of gypsum in already hardened concrete is expansive,

leading to cracking and disintegration of the concrete (Ekolu et al. 2014). However, concrete deterioration due to gypsum formation can be controlled or mitigated by incorporating supplementary cementitious materials such as fly ash into pervious concrete mixtures (Shabalala et al. 2017).

Recent studies have shown pervious concrete to be an effective reactive material for treating AMD. However, there are presently few or no published literatures available on the mechanisms responsible for concrete's efficacy in removing metals from AMD. As such, the present study focussed on this research subject. The investigation involved a batch reactor test done using pervious concrete comprising Portland cement CEM I 52.5R with or without fly ash. Microanalytical studies were done using X-ray powder diffraction (XRD), Fourier transform infrared spectrometry (FTIR), and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS).

Methods

Mine water, pervious concrete and zero-valent iron

The AMD samples used in the present study were obtained from two sources comprising an abandoned coal mine (TDB) and an underground gold mine (WZ). The batch test

was conducted for both WZ and TDB using pervious concrete. The materials used to prepare pervious concrete, comprising CEM I and 6.7 mm granite aggregate, were both supplied by Afrisam Cement (pty) Ltd. The FA used was obtained from Ash Resources (pty) Ltd. To prepare ZVI substrates, standard 100 mm cube moulds were filled with equal proportions of fine silica sand of size range 0.4 – 0.85 mm, coarse silica sand of size range 0.8 to 1.8 mm, fine ZVI grade GH 80 of size range 0.18 to 0.42 mm and coarse ZVI grade GH 18 of size range 1.0 to 1.4 mm. The ZVI material was supplied by BV Boksborg (Pty) Ltd. Each mixture was placed in an 8 L plastic container and filled with 3 L of WZ or TDB.

Batch tests

Six plastic containers, each of dimensions 130 mm by 215 mm were set up for the batch tests. In each container was placed a cube of CEM1, cube of 30% FA or ZVI-sand mixture of 1cm³. Three litres of WZ or TDB were added to each container. Vadapalli et al. (2008) observed that the active treatment and neutralization of AMD to circumneutral or alkaline pH was optimized when the ratio of AMD to reactive media was 3:1. Accordingly, a ratio of one concrete cube of 1 L by volume to 3 L of AMD was used in this study. Containers were tightly closed to ensure no evaporation took place. During the first 10 days, aqueous samples were collected once a day. Thereafter sampling frequency was decreased to once a week. The experiment was conducted continuously for a period of 43 days.

Analytical studies and microanalyses

Measurement of pH, conducted using MP-103 microprocessor-based pH/mV/Temp tester, was done immediately after collection of aqueous samples from batch tests. The pH electrode was calibrated using standard NIST-traceable pH 2.0, 4.0, 7.0 and 10.0 buffers. Collected samples were used for determination of the following cations: Al, Fe, Mn, Na, Mg, K, Ca, Mn, Fe, Co, Ni and Cu analysed using the PerkinElmer SCIEX (Concord, Ontario, Canada) ELAN® 6000 inductively coupled plasma-mass spectrometry system. SO₄ was determined by ion chromatography (Dionex QIC-IC).

Residues of the reacted adsorbents were taken from the batch reactors and used for XRD, SEM and FTIR microanalyses. Samples of the residues were oven-dried at 50 °C then used to prepare powder specimens for XRD analysis done using the Pan Analytical X-ray X'pert PRO PW3830 diffractometer. SEM examination of the residues was done using the TESCAN VEGA3SEM with AZtec EDS. Functional groups were determined using BX-II PerkinElmer FTIR equipped with the Universal Attenuated Total Reflectance (ATR) diamond crystal.

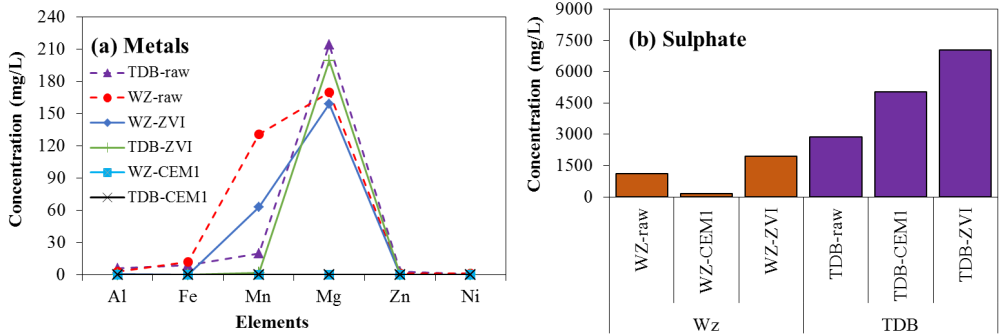
Results and Discussion

In the batch experiments, pH of raw AMD increased from initial values of 4.15 – 5.79 to pH = 6 to 8 for ZVI and pH = 9 to 12 for PervC. For both reactive media, a rapid increase of the pH was observed within the first 24 h of the experiment. The high pH values observed in the PervC-treated AMD is related to dissolution of portlandite from cementitious matrix which adds alkalinity into the system (Chandrappa and Biligiri 2016). The low final pH values attained for acidic water samples that were treated with ZVI as compared to those that were treated with PervC may be attributed to additional source of acidity provided by hydrolysis of Fe³⁺ in the ZVI samples, which lowers the pH.

The metal removal efficiency and changes in anion/cation concentrations were calculated as summarised in Table 1 and Fig. 1 for the PervC and ZVI reactive media. Average concentrations of elements over the period 10 to 43 days, were calculated for each element and then used to determine proportional decrease or increase from original AMD feed. Al, Fe, Ni, Co, Pb and Zn were successfully removed by both PervC and ZVI reactive media. The removal efficiency levels for Al, Mn, Mg and Cu were greater when AMD was treated with PervC as compared to treatment with ZVI. The lowest removal efficiency was observed in Mn and Mg concentrations when ZVI was used as a reactive media. After treatments using PervC or ZVI, the final concentration of SO₄ in treated effluent was always higher than that in the initial AMD feed.

Table 1 Contaminant removal efficiency levels of pervious concrete and ZVI reactive media.

AMD Type	Reactive Media	Al (%)	Fe (%)	Mn (%)	SO4 (%)	Mg (%)	Ni (%)	Co (%)	Cu (%)	Pb (%)	Zn (%)
WZ	CEM1	98	100	100	-24	96	97	95	96	99	100
	30%FA	99	100	100	-32	91	96	93	96	99	100
	ZVI	82	96	44	-51	12	95	95	59	99	94
TDB	CEM1	99	100	100	-75	99	98	99	76	99	100
	30%FA	99	100	99	-46	100	97	98	81	99	98
	ZVI	97	100	58	-95	16	96	98	80	99	100

**Figure 1** Contaminant removal and concentration changes after 43 days of pervious concrete or ZVI treatment.

Residues of reacted pervious concrete were taken from the batch reactors and examined by XRD. Figures 2 gives the XRD analyses done on residues of the reacted CEM I and 30%FA pervious concretes. Evidently, the most abundant product phase in all the mixtures is gypsum. The XRD spectra for TDB-CEM1 and TDB-30%FA also indicate the presence of thernadite (Na_2SO_4) as a minor mineral phase in both concrete mixtures. The WZ-30%FA residues gave a similar XRD pattern as TDB-30%FA of Figure 2a, generally showing an intermixture of metal precipitate complexes including calcium, strontium, aluminium, silica ($\text{CaSrAl}_2\text{SiO}_7$). The calcite observed in Figure 2a is likely to have formed due to exposure of the solid samples to the atmosphere, during sample preparation. The functional groups formed in the reacted pervious concrete following its exposure to AMD, are shown in Figure 2b. The FTIR spectra indicate the presence of vibrating carbonate stretches of calcite at a wavenumber 2349 cm^{-1} . Stretches at the wavenumber 1000 cm^{-1} are attributed to gypsum (Prasad

et al. 2006). These findings provide evidence for the formation of gypsum and calcite - bearing precipitates, and are consistent with the observations from XRD analyses (Figure 2a). Goethite (FeOOH) was identified as the mineral phase formed in both WZ-ZVI and TDB-ZVI, as seen in Fig.3. At higher value of pH, the ferric hydroxides (FeOOH , FeOH_3) may be created on the surface of ZVI, on which metals in cationic form may be sorbed. The iron corrosion products appear as a result of Fe0 oxidation to Fe^{2+} and then to Fe^{3+} (Suponik and Blanco 2014).

Concrete's mechanisms for removal of metals

Findings from the present study show that concrete's removal of metals from AMD occurs through two simultaneous processes. The initial removal step is the precipitation of metal (oxy)hydroxides owing to rise in the pH of AMD as driven by $\text{Ca}(\text{OH})_2$, a cement hydrate which is massively present in concrete. Simultaneous to metal precipitation, is the formation of gypsum as a by-product upon

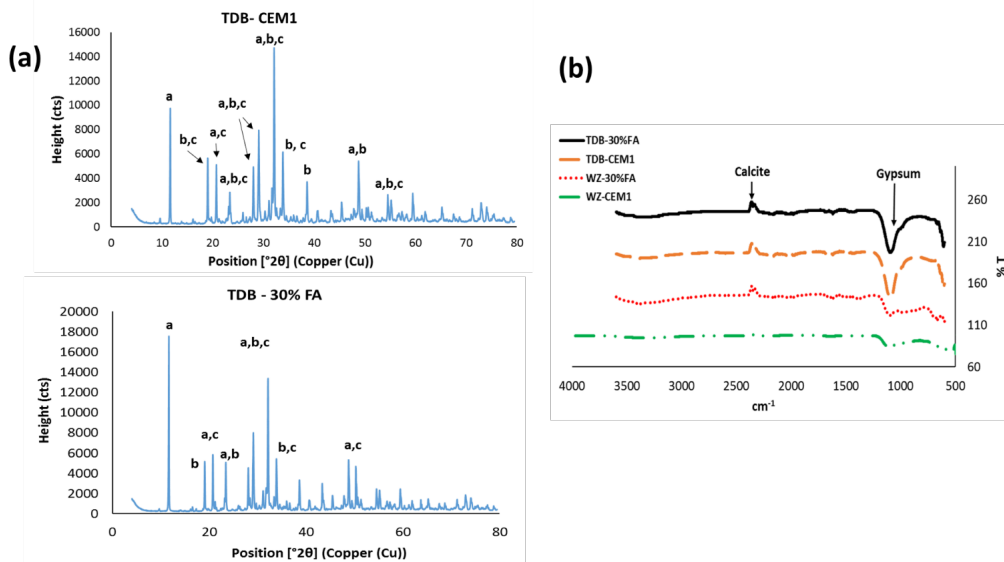


Figure 2 (a): XRD analysis on residues of TDB-CEM1 and TDB-30%FA concrete mixtures: a - gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$); b- Calcium strontium aluminium silicate ($\text{CaSrAl}_2\text{SiO}_7$); c - Calcite (CaCO_3). (b) FTIR patterns of TDB-30%FA, TDB-CEM1, WZ-30%FA and WZ-CEM1 residues of pervious concrete.

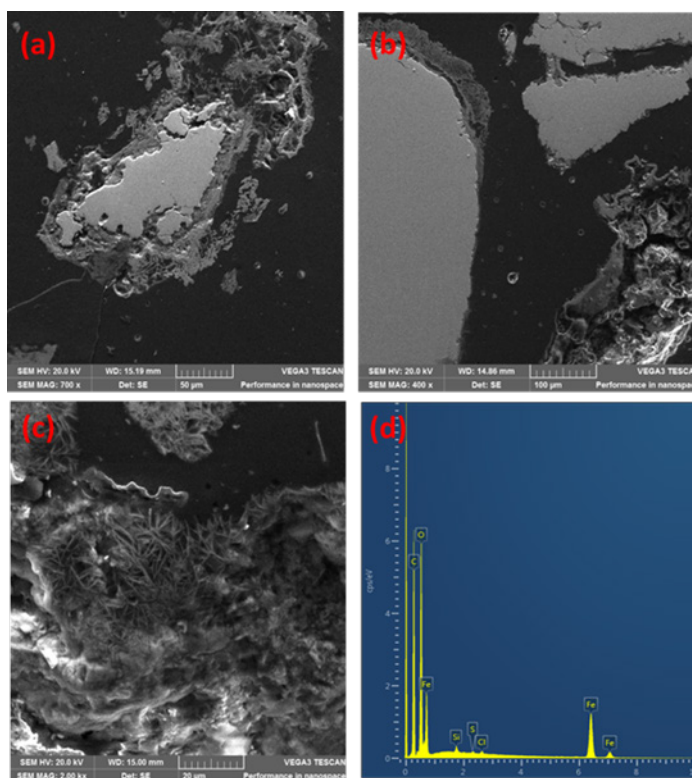


Figure 3 SEM examination of surface coating for ZVI: (a) reacted WZ-ZVI residues, (b) reacted TDB- ZVI residues, (c) close up of ZVI showing needle-like/acicular shaped crystals typical of goethite (FeOOH), (d) EDS spectra with high intensities of Fe and O which supports the presence of FeOOH .

the reaction of $\text{Ca}(\text{OH})_2$, with sulfuric acid from pyrite oxidation and with the sulfate in AMD. The gypsum by-product formed, in turn adsorbs the metal precipitate complexes through physical adsorption processes.

Conclusions

A batch reactor test was done to compare the effectiveness of using pervious concrete for treating acid mine drainage relative to use of the conventional zero-valent iron system. The calcium hydroxide hydrate in pervious concrete reacts with AMD, increasing its pH to a high alkaline level, in turn leading to precipitation of metals out of solution. The removal rates for Al, Fe, Mn, Mg, Ca, and Cu were 95 to 100% when acid mine drainage was treated using pervious concrete as compared to 12 to 99% for zero-valent iron treatment. Gypsum is formed as a by-product upon the reaction of calcium hydroxide with sulfuric acid from pyrite oxidation and with the sulfate in AMD. The gypsum formed, adsorbs the metal oxy(hydroxide) precipitates through physical adsorption processes. Accordingly, the mechanisms of pervious concrete's removal of metals from AMD comprise the pH-driven metal precipitation occurring simultaneously with physical adsorption of the precipitates onto the surface of PervC and gypsum by-product formed.

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