Comparative Study of Leaching of Metals from Pervious Concrete Incorporating Coal Fly Ash and Ground-Granulated Blast-Furnace Slag

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Abstract

The leaching of metals from pervious concrete incorporating Portland Cement (CEM I) fly ash (30% FA) and Ground-granulated blast-furnace slag (50% GGBS) could have potential adverse effects on human health and the ecosystem. Leaching characteristics of metals from these concretes were investigated using the Toxicity Characteristic Leaching Procedure (TCLP), batch, and column tests. Results indicated that concentration levels of all regulated elements in the leachates were lower than the TCLP leachate quality criteria. However, CEM I and FA concrete samples showed higher metal leachability than GGBS samples with Cr6+ levels being higher than the specified limits which pose an environmental risk.

Keywords: Acid mine drainage, Leaching, Pervious concrete, Coal fly ash, Ground-granulated blast-furnace slag

Introduction

If left untreated, Acid Mine Drainage (AMD) can contaminate ground and surface watercourses, damaging the health of plants, humans, wildlife, and aquatic species. The high cost of AMD remediation has resulted in the search for alternative liming substitutes which are low cost, readily available, and easily regenerated. Pervious concrete has attracted attention as a result of its low costs, environmental sustainability, and its effectiveness in treating polluted or acidic water (Shabalala *et al*., 2017, 2019). However, it is structurally weaker and less durable than conventional concrete. Therefore, natural or chemical admixtures have been added to pervious concrete to increase its strength and durability. Dell'Orso *et al*. (2012) reported that the use of mineral additions in cement reduces the amount of Portland cement clinker that is consumed, reduces the related CO2 emission, a vast amount of energy is saved and the natural resources involved in cement production such as limestone and clay are also preserved. Partial replacement of pervious concrete with fly ash has been shown to improve the workability of fresh concrete and the mechanical strength and durability of normal porous concrete. Fly ash could be utilized for a cleaner production of pervious concrete possessing compatible hydrological properties and pollution control potential, compared to ordinary pervious concrete (López-Carrasquillo and Hwang, 2017). Ground Granulated Blast Furnace Slag (GGBS) which is a by-product extracted from blast furnaces used to produce iron is commonly used as binder replacement materials bearing a much lower carbon footprint and can be highly effective in enhancing the workability, durability, and corrosion resistance of concrete structures (Yeung *et al*., 2019). To lower the CO2 emissions and the consumption of natural resources, waste materials like ashes, slags, and alternative aggregates, are increasingly being used in cement and concrete production. But these materials are often characterized by a high content of trace elements and potentially hazardous metals which are of environmental concern (Hartwich and Vollpracht *et al*., 2017; Dell'Orso *et al*., 2012). The release of metals into the environment when cement or concrete products are exposed to water, soil, and air, may result in a threat to environmental safety and human health. It is, therefore, necessary to evaluate and analyze the leaching of metals from cement products. In view of using fly ash and GGBS as a replacement for cement in concrete mixes, pervious concrete utilizing fly ash and ground-granulated blast-furnace slag was developed. The present study aims to investigate the metal leaching characteristics of porous concrete. Although pervious concrete has been shown to be effective in reducing the loading of metals and organic contaminants in acid mine drainage, the leaching potential of metals (Al, Fe, and Mn) from pervious concrete and the capacity of pervious concrete to immobilize trace elements such as Ba, Cd, Cr, Co, Cu, Ni, Pb, Zn, Sr and V which are common contaminants in acid mine drainage is not well understood. The experimental results of pervious concrete incorporating FA and pervious concrete incorporating GGBS will be compared to the results of pervious concrete made with ordinary Portland cement paste. In addition, microstructural analysis using X-ray diffraction (XRD) will be used to investigate changes in mineral phases of the concrete during leaching.

Materials and methods

Concrete mixtures

PERVC was made using ingredients consisting of Portland cement CEM I 52.5R with or without 30%FA, 50%GGBS and 6.7 mm granite aggregate. Class F fly ash, Portland cement and GGBS were obtained from Ash Resources Ltd, Pretoria Portland cement company and Best cement trading, respectively. Class F fly ash was used as classified in the standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete (ASTM C 618, 2015). Three concrete mixtures were prepared in which the fly ash and GGBS content in concrete was 30% and 50% by mass of the total cementitious materials, respectively. A water-to-cementitious ratio of 0.27 was used for all mixes. Fresh concrete was cast in 100 mm cubes, left to dry for 24 h, then demolded and left in a curing bath for 28 days.

Toxicity Characteristic Leaching test

The U.S. EPA Regulatory method 1311-Toxicity Characteristic Leaching Test (TCLP) was used as a reference to investigate the leaching characteristics of metals and trace elements from pervious concrete with and without fly ash and GGBS replacement. The concrete cubes were sliced to approximately 30 x 30 x 10 in thickness, and each weighed 20 g (± 2). Each of the concrete samples was placed in a 1000 mL glass beaker into which 400 mL of 0.1N acetic acid with pH 2.84 was added, as shown in Figure 1. The liquid-solid ratio was 20:1 with a contact time of 24 h. The pH, EC and TDS of resultant leachate was measured immediately following collection using a MP-103 microprocessor-based pH/mV/Temp tester and thereafter analyzed for Al, B, Cd, Cu, Co, Fe, Pb, Ni, Zn. Water quality criteria for leached metals will be based on the EPA extraction procedure toxicity test (EP Tox). The criteria for metals are set at 100 times the National drinking water standards. If the leachate from a material exceeds these criteria, then the material is considered hazardous (Zhang *et al*., 2001). Regulated concentration levels of metals specified in the TCLP leaching test are given in Table 1. The Transportation of Dangerous Goods Regulations (TDGR) which is a TCLP Canadian Equivalent is also presented in the table.

Figure 1 *Toxicity characteristics leaching tests.*

Table 1 Leaching quality criteria (Zhang et al.*, 2001)*

Metal	As	B	Ba	Cd	Cu	Hg	Pb	Se	Zn
EPA,USA, TCLP (mg/L)	5	-	100	1	-	0.2	5	1.0	-
TDGR, Canada (mg/L)	5	500	100	0.5	100	0.1	5	-	-

Batch reactor experiment

The AMD used was obtained from an abandoned coal mine. Each standard 100 mm concrete cube (CEM1, 30%FA and 50% GGBS) was placed in a 4 L plastic container and filled with 3 L of AMD. Samples were collected each day for the first 10 days and thereafter once a week for a total of 43 days.

Column experiment

The main objective of this test is to study long-term leaching behaviour and to determine the optimum quantity of metals that leached out from CEM1, 30%FA and 50% GGBS. Four concrete cubes of CEMI, 30%FA and 50%GGBS were placed in separate columns. The columns used in this study are 500 mm in height and have an internal diameter of 100 mm. An AMD sample was pumped at a flow rate of 0.35 ml/min. Leachate samples were collected daily for the first 3 months, then once every third day and thereafter, to once a week for a total of 175 days. Concentrations of B, Cr, Cd, Co, Cu, Ni, Pb, U and Zn were determined using the PerkinElmer SCIEX (Concord, Ontario, Canada) ELAN® 6000 inductively coupled plasma–mass spectrometry. The concentration of Cr^{6+} was determined using Ion Chromatography, Dionex QIC-IC instrument.

Results and Discussion

Effect of the pH on leaching of metals

Batch experiments showed an increasing trend toward higher concentrations of major elements (Ca, Si, Al, Mg) and trace metals (Cu, Pb and Zn) associated with lower pH values. The observed major element and trace element (Cr, Cu, Pb and Zn) leaching behaviour is best explained by the dissolution/precipitation of concrete phases and surface complexation, respectively. Water passing through pervious concrete has an increase in pH because of reactions with portlandite and calcite in the porous cement. Generally higher pH values reduce metal loading but trace metals do tend to increase to some extent at pH > 9 (Solpuker *et al.*, 2014)

Toxicity characteristic leaching Procedure (TCLP) test results

The concentrations of As, B, Ba, Cd, Pb, Ni, Se, Hg, and Zn in the leachate from the CEM I, 30%FA and 50%GGBS were below the limits specified by EPA, USA and the DGTR, Canada. Fly ash and GGBS concrete samples showed higher metal values than Portland cement concrete samples except for Ni. The values of Ni for fly ash and GGBS were lower than those of Portland cement concrete. Concrete containing fly ash and GGBS showed higher concentrations of Cu, B, Co, and Se while higher Fe and Zn values were recorded for Portland cement (Fig 2.1). Cu in 30%FA and 50% GGBS concrete mixtures, which had a concentration of 0.8570 and 4.65 mg/L, respectively, is the only metal that showed high leachability in the test. Mineralogical characterization of the concrete mixtures (Fig 2.2) was carried out at 175 days using X-ray powder diffraction (XRD). The analysis was performed with a Pan Analytical X-ray X'pert PRO diffractometer. The most abundant product phase in all the mixtures was gypsum ($CaSO_4{\cdot}2H_2O$). Plain pervious concrete (CEM 1) was mainly composed of gypsum, thernadite (Na2SO4) and quartz (SiO_2). Ordinary Portland cement primarily consists of calcium and silicon compounds with lesser quantities of iron and aluminium compounds. The XRD spectra for 30% FA indicate the presence of gypsum and Glauber's salt (Na_2SO_4) while that of 50%GGBS shows gypsum and quartz as the main reaction products. The release of metals occurs owing to the dissolution of these minerals.

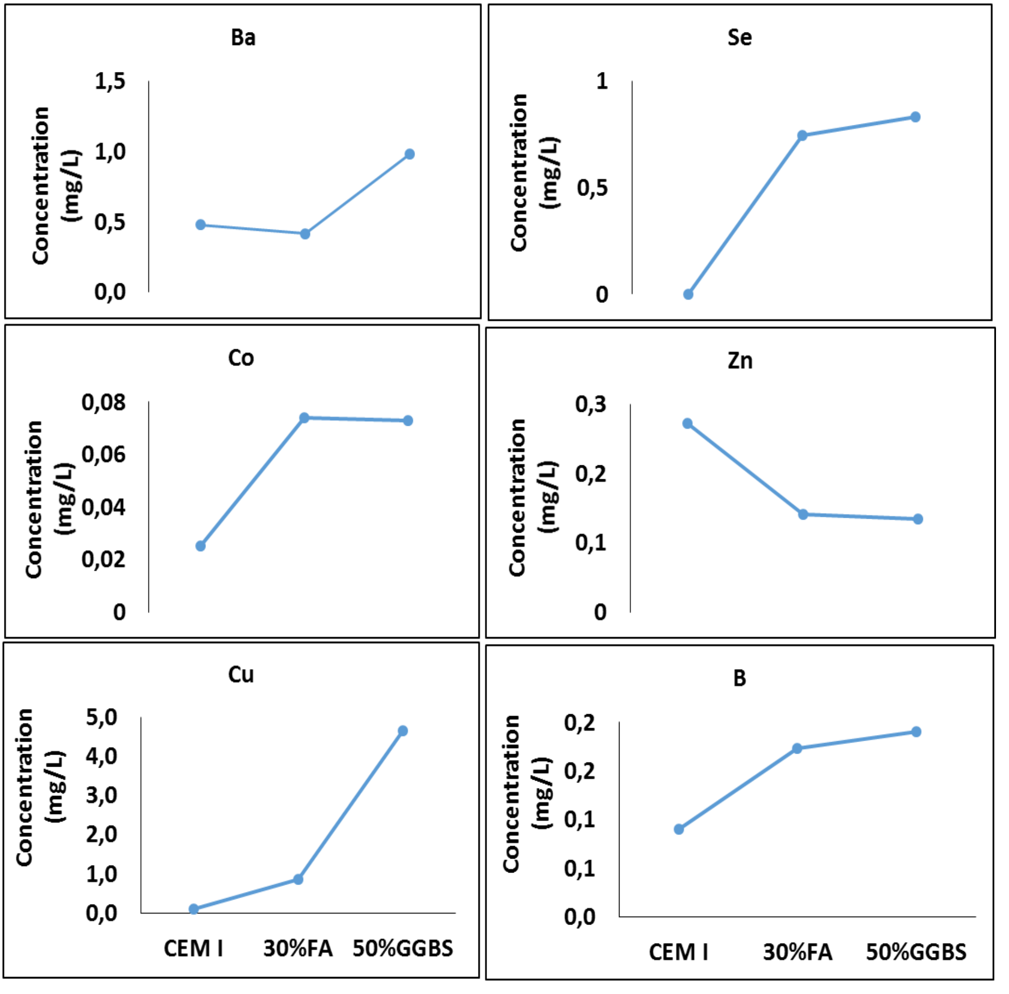

***Figure 2.1** General trends in the leaching behaviour of selected elements after 24 hours of contact time with the concrete mixtures.*

Batch reactor experiment

After 43 days of batch tests using acid mine drainage, the elements Ni, Co, Cu, Cd , Pb, Zn B, U and As in treated mine drainage were maintained at levels below those in the untreated acid mine drainage. The concentrations of metals (Ni, Co, Cu, Cd, Pb, Zn, B and As) in the leachates from concrete mixtures were lower than the limits specified by EPA (1986), WHO (2006) or SANS 241 (2015). In general, the 30% FA concrete leachate showed similar or higher metal values than CEM1. FA concrete samples showed higher leachability of Cr and Cr^{6+} when compared to CEM1 and 50% GGBS concrete samples. A slightly higher concentration of Se leaching was observed with CEM1.

Column experiment

After 175 days of column leach test using acid mine drainage, the concentrations of metals (Ni, Co, Cd, Pb, and As) in the leachates from plain Portland cement (CEM 1), concrete with fly ash (30% FA) and concrete containing GGBS (50% GGBS) were lower than the limits specified by EPA (1986), WHO (2006) and SANS 241 (2015) therefore showed no risk for the environment if they leach out from the pervious concrete and

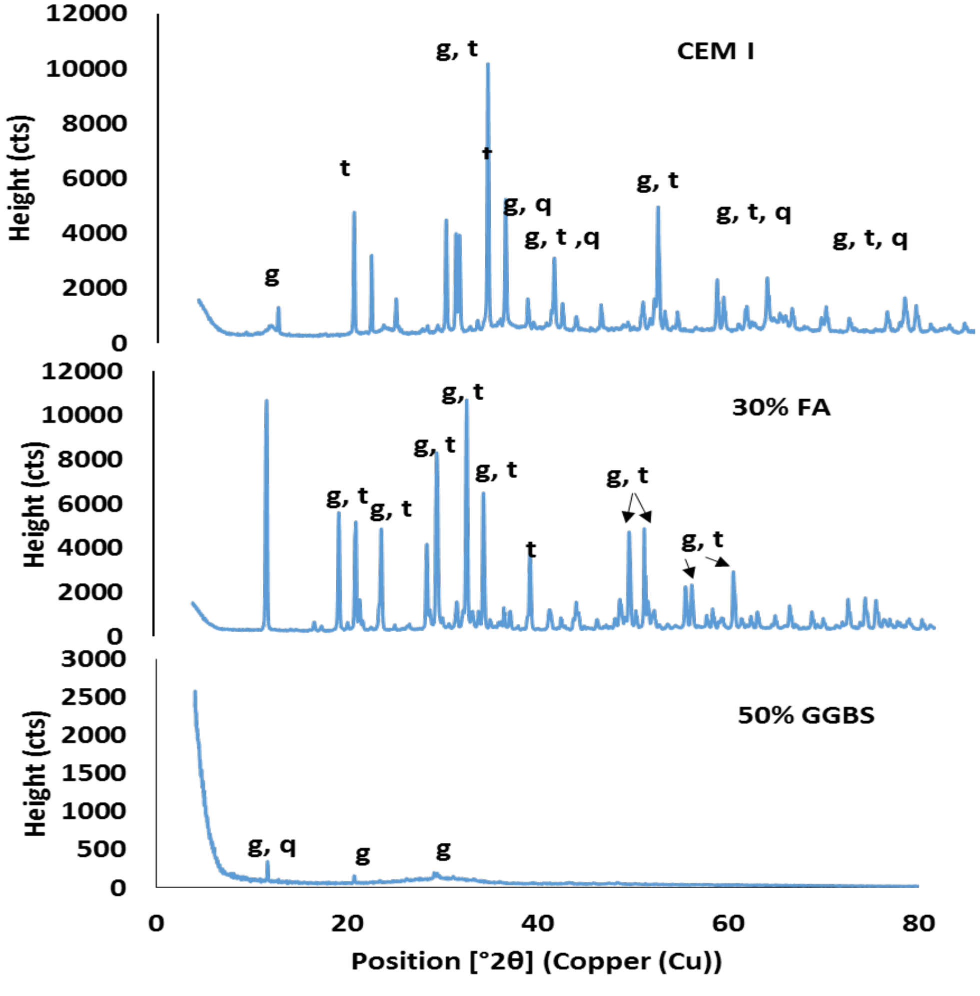

Figure 2.2 *XRD pattern of residues from CEM I (a) 30%FA (b) and 50% GGBS (c) at 175 days in the reactor column where g-gypsum; q-quartz; t-thernadite.*

fly ash matrix. The concentration of these metals showed no trend with time, being at or below detection limits for the duration of the tests. The concentrations of Zn and Cu in CEM 1 and 30%FA were higher than the limits specified by NWA (1999) and therefore pose a potential environmental risk. This is in agreement with the findings of Pöykiö *et al*. (2016) that Zn concentration in the fly ash is generally elevated. Fly ash concrete samples showed higher leachability of Co, Zn, and Ni when compared to CEM1 concrete samples. The concentrations of Co, Zn and Ni were 0.0050 and 0.0114, 0.7142 and 0.7740, 0.000 and 0.0685 mg/L, for CEM1 and 30%FA, respectively. The concentration of Cr in all three concrete mixtures was lower than the recommended limits of 2 mg/L (EPA, 1986). CEM1 and 30%FA showed higher leachability of Cr^{6+} with average concentrations of 0.209 and 0.067 mg/L, respectively, owing to leaching from the cement and fly ash materials used in the pervious concrete mixtures. These values are higher than the recommended maximum concentration specified by the World Health Organisation (WHO) of 0.05 mg/L and therefore pose an environmental risk. For GGBS, the concentration of Cr6+ was 0.059 mg/L indicating that leaching did not take place. The element release therefore strongly depends on the concrete

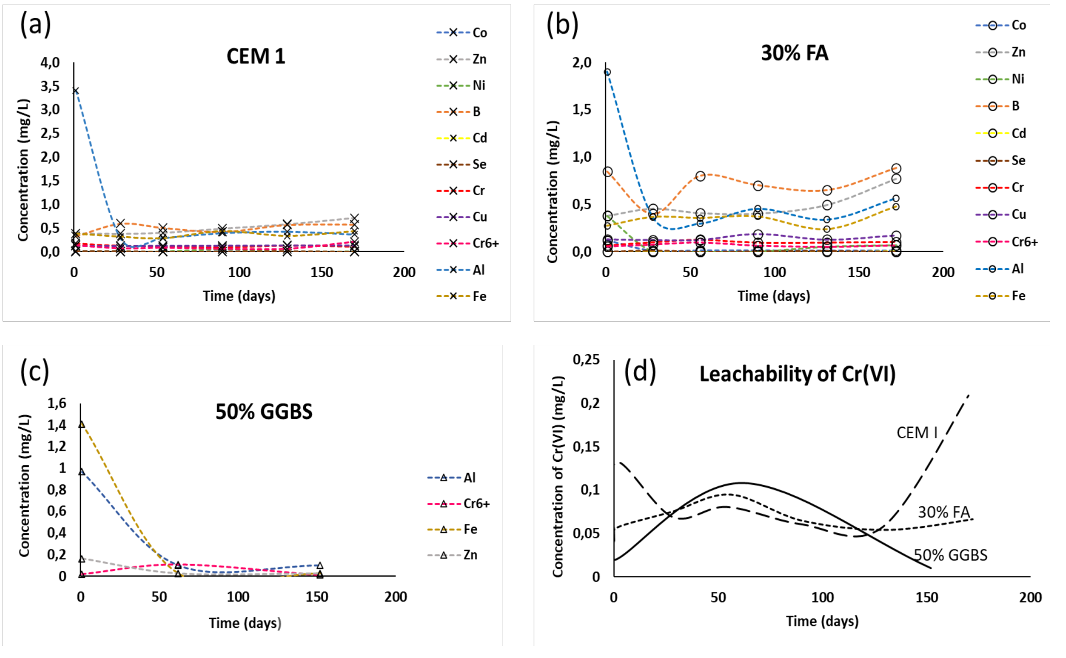

Figure 3 Concentrations of metals leached from CEM I, 30% FA and 50% GGBS concrete samples.

composition and trace element content. For example, the higher chromium content of the cement results in higher pore solution concentrations and a higher release during leaching (Hartwich and Vollpracht, 2017). Low risk is caused by eight trace metals (Co, Cd, Ni, B, Pb, Zn, Be, As) in CEM1, six trace metals (Co, Cd, Ni, Pb, Be, As) in 30%FA and three metals (Al, Fe, Zn) in GGBS. In general, for both batch studies and column studies, the concentrations of metals leached when GGBS was incorporated into the cement were less than that observed when plain Portland cement or cement incorporating 30%FA were used.

Conclusion

The results showed that none of the metals in the leachates from CEM I, 30% FA and 50% GGBS concrete samples exceeded the regulated levels specified in the Toxicity Characteristic Leaching Procedure (TCLP) test therefore are considered stable with respect to leachability and show no obvious environmental risk. Batch and column studies showed that the concentrations of metals leached in cement containing slag (50% GGBS) were less than that observed when plain Portland cement (CEM 1) or cement incorporating fly ash (30%FA) were used. Cu, Fe, Se, B and Zn showed increasing concentrations in the leachate with time although they were below the level specified in water quality guidelines. The Cr^{6+} levels in CEM 1 and 30% FA concrete samples were higher than the specified limits. Therefore, Cr6+ in cement products should be controlled to avoid its potential environmental risk.

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