Cement and Concrete Research 92 (2017) 56–65

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: www.elsevier.com/locate/cemconres

Resistance of geopolymer and Portland cement based systems to silage effluent attack

Timothy A Aiken *, Wei Sha, Jacek Kwasny, Marios N Soutsos

School of Natural and Built Environment, Queen's University Belfast, Stranmillis Road, Belfast, BT9 5AG, UK

ARTICLE INFO

Article history:
Received 7 July 2016
Received in revised form 17 October 2016
Accepted 11 November 2016
Available online xxxx

Keywords:
Organic acids (D)
Fly-ash (D)
Ground granulated blast-furnace slag (D)
Microstructure (B)
Durability (C)

ABSTRACT

Traditional Portland cement (PC) concrete has been used for many years in the agricultural industry for the construction of silos and silage effluent storage facilities. However, the acidic nature of the silage effluent produced by silage has led to severe degradation of PC concrete which in turn has significant environmental and financial implications. This study compares the resistance of PC and geopolymer (GP) mortars and pastes to silage effluent over 12 months. The GP samples displayed increased resistance to silage effluent in terms of mass and strength loss. Analysis of microstructure suggests that the increased stability of the reaction products is the main factor behind increased silage effluent resistance when compared with PC. It was also found that blends of pulverised fuel ash (PFA) and ground granulated blast furnace slag (GGBS) with a higher PFA content may offer increased long term silage effluent resistance due to the nature of the main binder gel produced in PFA dominant systems.

1. Introduction

Within the agricultural industry, silage effluent is known to cause damage and deterioration to concrete structures such as silo walls, floors and storage tanks [1]. Silage effluent is produced as a result of storing grass as winter feed for livestock [2]. The grass is placed in concrete silos, compacted and sealed. It then undergoes a fermentation process converting sugars to acids and producing silage effluent [3]. The resulting effluent typically contains lactic and acetic acid and has a pH value of approximately 4.0 [4–6]. The concentration of lactic and acetic acid in silage effluent is typically in the range of 5–44 g/l and 1–5.5 g/l respectively [7]. In recent years, the practice is to allow the grass to wilt or dry out as much as possible before storage. This means there is less effluent produced during fermentation because there is less moisture available [8]. Although this has helped reduce the volume of effluent produced, the problem has not been eliminated because the reduced effluent volume can still be sufficient to cause significant concrete damage. Furthermore, it is not always possible to allow grass to wilt before storage due to unpredictable weather and time constraints [8].

Portland cement (PC) concrete structures have been suffering serious degradation due to effluent attack for many years. This degradation process has been observed to erode concrete progressively and may be accelerated by mechanical actions such as high pressure cleaning and machine traffic [9]. The reactions between the acidic effluent and cement hydrates produce calcium salts which are highly soluble [10]. This allows the porosity of the matrix to increase and the mechanical strength to decrease while at the same time the concrete cover is being degraded which may lead to corrosion of steel reinforcement and structures being destroyed [11]. There are significant environmental and financial consequences of such damage [9]. The escape of silage effluent can result in serious surface and groundwater pollution [8]. Silage effluent must be effectively managed and collected because it poses a considerable pollution threat [12]. Silage effluent has a biochemical oxygen demand of up to 200 times that of domestic sewage and has the potential to kill large quantities of aquatic life [13]. When this type of pollution occurs, significant financial penalties can be incurred as well as the cost to repair or reconstruct damaged storage facilities which allowed the silage effluent to escape. Therefore, there is a need for alternative materials which provide increased resistance to silage effluent attack.

Global issues such as climate change, the depletion of the earth's resources and pollution are causing many countries to commit to reducing their environmental impact, specifically their CO_2 emissions [14]. The production of Portland cement is an energy intensive process [15] and approximately 0.7–1.1 tonnes of CO_2 are emitted for every tonne of cement produced [16]. As a result, the cement industry contributes approximately 7% of worldwide CO_2 emissions [17]. However, the use of alternative binder materials can reduce CO_2 emissions associated with concrete production. The use of replacement materials such as pulverised fuel ash (PFA) and ground granulated blast furnace slag (GGBS) in place of PC is estimated to reduce CO_2 emissions associated with concrete by up to 80% [18]. GGBS is obtained from the production of iron and is widely used in the production of alkali activated cements [19]. PFA is a residue obtained from coal combustion at power plants

---

* Corresponding author.
E-mail address: taiken02@qub.ac.uk (T.A. Aiken).

http://dx.doi.org/10.1016/j.cemconres.2016.11.015
0008-8846/

Table 1
Oxide compositions obtained by XRF for raw materials - PFA, GGBS and PC.

Material	CaO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	SO_3	MgO	TiO_2	MnO	LOI
PFA	2.24	46.78	22.52	9.15	0.89	4.09	0.90	1.33	1.05	0.05	3.57
GGBS	43.72	29.38	11.23	0.36	1.05	0.93	1.76	6.94	0.67	0.51	2.40
PC	63.01	20.21	4.79	2.78	0.19	0.59	2.60	1.93	0.27	0.08	3.16

and is also considered an environmentally friendly source material [20]. However, PFA is increasingly considered a valuable material. In 2014, 70% of the PFA produced in the UK was used in the manufacture of construction materials [21]. Nonetheless, there are approximately 114 million tonnes of PFA stockpiled accessibly in the UK [22], while in many countries around the world, utilisation of PFA is a major problem with as little as 7% being utilised effectively [23].

Individually alkali activated GGBS and alkali activated PFA have been studied by many authors. The acid resistance of these two binder types has also received much attention [24–28]. More recently the possibility of blending two waste or by-products together to form one binder has been investigated [29]. Therefore, the acid resistance of blended PFA and GGBS binders is less well known. Furthermore, the resistance of PFA and GGBS based geopolymer (GP) cements and concretes to silage effluent attack has received very little attention within the research community. However, a study was carried out recently which suggests that alkali activated GGBS displays increased resistance to organic acid collected from silos compared with traditional PC [30].

In this study two blends of GP mortars and pastes using PFA and GGBS as binder materials have been exposed to silage effluent for 12 months. PC samples have also been studied in order to compare performance and investigate the mechanism of attack on each binder.

2. Experimental methods

To investigate the resistance of GP and PC based systems to silage effluent attack, mortar samples were prepared and submerged in silage effluent for 12 months. The samples were monitored visually and their mass change and compressive strength was also recorded. Control samples were submerged in water for 2 months for compressive strength comparison. Paste samples were also prepared and submerged in silage effluent for 12 months in order to carry out microstructural analysis to gain an understanding of the mechanism of attack. The paste samples were analysed by X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

2.1. Materials

The PFA used in this study was a class F fly ash sourced from Power Minerals Ltd., UK and the GGBS was supplied by Hanson group, UK. Portland cement CEM I 42.5N, produced by Quinn Cement in Northern Ireland, and conforming to the standards of BS EN197-1:2011 [31] was used as PC. The oxide compositions for PFA, GGBS and PC obtained by X-ray fluorescence (XRF) are displayed in Table 1. The XRD spectra of the binder materials PFA, GGBS and PC are shown in Fig. 1. The main crystalline phases present in PFA include quartz, mullite and hematite. However, GGBS is almost completely amorphous with a broad peak or hump between (2θ) 25 and 35°. The PC used in this study has many crystalline phases including alite, belite, aluminate, brownmillerite and gypsum. The PFA and GGBS binders were activated by solutions of sodium silicate and sodium hydroxide. The sodium silicate solution was supplied by Fisher Scientific and consisted of 12.8% Na_2O, 25.5% SiO_2 and 61.7% water. The sodium hydroxide solution was prepared at

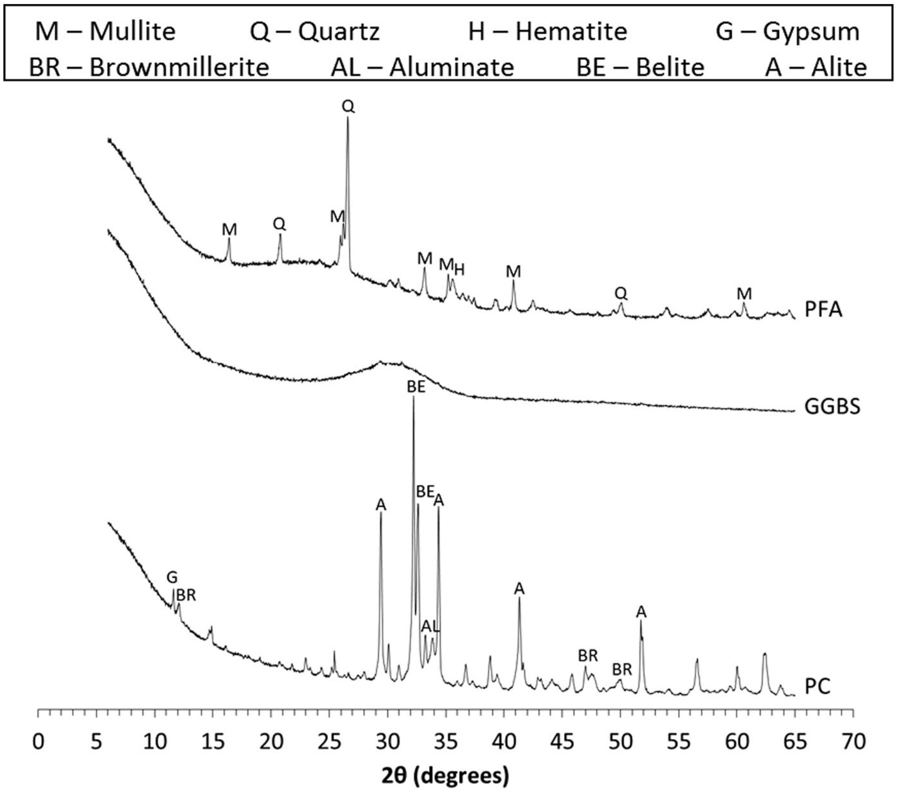

Fig. 1. XRD spectra for raw materials - PFA, GGBS and PC.