PERFORMANCE OF ADMIXTURE AND SECONDARY MINERALS IN ALKALI ACTIVATED CONCRETE

Sustaining a concrete future

Arno Keulen

/ Department of the Built Environment





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PERFORMANCE OF ADMIXTURE AND SECONDARY MINERALS IN ALKALI ACTIVATED CONCRETE

-Sustaining a concrete future-

PROEFSCHRIFT (thesis)

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. P.F.T. Baaijens, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op maandag 26 februari, 2018 om 11.00 uur in de Senaatszaal van het Auditorium gebouw.

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'Let your imagination be inspired by science'

Summary

This thesis addresses the use of secondary minerals (slags and ashes) and a plasticizing admixture in environmentally friendly cement-based systems for the production of 'sustainable' building materials with improved technical and 'environmental' performance. Here, "cement based systems" is referred to an alkali activated slag-fly ash binder and Portland blast furnace slag cement (CEM III). Further "slags" are referred to ground granulate blast furnace slag (GGBS) and ashes are referred to class F type pulverized coal fly ash (PCFA) and municipal solid waste incinerator (MSWI) bottom ash. The main research is divided into two different directions, namely the material technical and 'environmental' performances:

Technical performance

- Design and development of an alkali activated GGBS-PCFA binder in combination with a plasticizing admixture, to improve the fresh and hardened material state of alkali activated concrete mixtures.
- Physical/chemical understanding of the admixture within an alkali activated GGBS-PCFA system.
- Technical performance of MSWI bottom ash as secondary aggregate replacing coarse primary aggregate (gravel), in the production and design of cement based concrete mixtures.

Environmental performance

- Leaching behavior and mechanisms of heavy metals and salts of single secondary minerals (GGBS, PCFA and untreated and treated MSWI bottom ash fractions) in natural and alkaline environment (as a function of material pH).
- Leaching behavior of oxyanionic metals of alkali activated GGBS-PCFA materials influence on the mixture design, from monolithic (concrete) and granular (aggregate) state materials.
- Leaching behavior of heavy metals and salts of Slag cement (CEM III) concrete mixtures, replacing natural aggregate by treated MSWI bottom ashes from monolithic (concrete) and granular (aggregate) state materials.
- Modeling of pH dependent leaching behavior of elements (metals and salts) of single secondary minerals (slags and fly ashes before and after treatment).
- Modeling of pH dependent leaching behavior of elements (metals and salts) of granular state materials, as aggregates in their second life phase when concrete products are recycled.
- Describing leaching behavior and related adsorption and complexation mechanisms in concrete mixture predicting the potential leaching of future aggregate when subjected to carbonation.

Research was performed on both alkali activated material (AAM) and Portland cement-based systems in order to gain more understanding on their physical/chemical mechanisms. Specifically, research on admixture use as system modifier in an alkali activated GGBS-PCFA binder system for the production of AAM is addressed, by focusing on its working mechanisms (calcium complexation and adsorption mechanisms). Additionally, obtained results were implemented to design AAM concrete mixtures, with a varying admixture content as variable. These AAM concrete mixtures were analyzed on their fresh (e.g. slump) and hardened material state properties in time such as, compressive strength and porosity. Furthermore, various durability aspects including chloride migration, material resistivity and microstructure development are investigated. Finally, based on the gained knowledge, a novel admixture modified alkali activated GGBS-PCFA concrete product (ultra-lightweight concrete) was designed, applying a concept which was originally developed for Portland cement concrete mixture design. This novel concrete product shows a moderate compressive strength ranging between 8 to 10 MPa in combination with a very low thermal conductivity ranging between 0.07-0.11 W/(m·K). Furthermore, fundamental in combination with practical research was performed on the treatment, material characterization and application of MSWI bottom ash as secondary aggregate for concrete mixtures. A secondary coarse aggregate for replacing primary aggregate from 0 to 100 wt.% in Slag cement concrete mixtures (earth moist pavement- and curb stones) was investigated. Both the aggregate production and concrete mixture production were done based on large pilots to support the technical and practical potential and high performance of treated (optimized) bottom ash aggregate.

Apart from the so-called 'technical' performances, the 'environmental' performances of the secondary minerals (slags and fly ashes) and that of concrete mixtures within a granular and monolithic state were assessed in chronological steps:

- Firstly, element leaching of the secondary minerals in their natural (initial) condition was analyzed (i.e., GGBS, PCFA and the initial MSWI bottom ash fractions). This led to an improved understanding of their physical/chemical leaching behavior and related mechanisms of potential toxic elements (heavy metals and salts), at which typically the highly soluble salts (chloride and sulfate) and oxyanion metal species, often abundant in alkaline secondary minerals, showing a relatively high leaching potential. Furthermore, a comparison of the overall leaching of these minerals with the regulatory Dutch Soil Quality Decree (SQD) leaching limits was examined, in case these minerals are applied as granular state building materials for open application.
- Secondly, leaching of specifically oxyanion metal species (As, Se, V, Mo and Cr) of monolithic and granular state AAM was examined, under various conditions by changing e.g. GGBS-PCFA precursor composition, binder content, activator

concentration, L/B ratio and curing time and the related compressive strength. All the tested monolithic state (concrete) materials show a very low element leaching potential. Typically for the granular (aggregate) state materials, a higher fly ash binder content and a higher activator concentration are of significance to increase the leaching of certain oxyanionic metals species. However, the leaching of aggregate of AAM fits overall in the 5 to 95% range of oxyanion leaching from blended Portland cement materials (containing GGBS and PCFA as supplementary cementitious material). In addition, the leaching of monolithic and granular state materials was performed on the Portland cement based mixtures, having an increased MSWI bottom ash aggregate to natural coarse aggregate replacement level. No significant differences between the reference mixtures (containing only primary gravel) and mixtures with an increased bottom ash aggregate content are observed. All mixtures comply with the regulatory leaching limits (Dutch SQD standard) for granular and monolithic state building materials for open application.

• Thirdly, pH dependent leaching behavior of elements (metals and salts) of the single secondary minerals (slags and fly ashes) and of granular state materials were analyzed and modelled to explain the physical/chemical mechanisms (i.e., adsorption and or complexation reaction mechanism). This pH dependent leaching approach was applied to predict the leaching behavior as a potential indication of future aggregate leaching under influence of carbonation, which is known to occur in the second life phase of recycled concrete.

Overall, the use of secondary minerals as binder or aggregate material, in cement based system for the production of sustainable ('green') concrete materials is proven to have a high potential, by meeting comparable technical and environmental performances obtained from traditional systems with primary materials. Especially for the production of AAM, modification by admixture is of significance to control the system and to enhance the fresh and hardened material state and related concrete durability performance. This in the end can help future development and practical application of alkali activated binder and concrete technology to become more mature.

Preface

THIS IS IT ofwel: basta! Na jaren werken is de wetenschap weer een stapje verder gekomen, en vele pagina's tekst rijker. Het opzetten en uitvoeren van het onderzoek en het schrijven van deze thesis was fascinerend en verruimend voor mijn ontwikkeling en inzicht in leven. Dit onderzoek heeft een sterke bijdrage geleverd aan de ontwikkeling en praktische implementatie van secundaire mineralen en het gebruik van alkali geactiveerde bindmiddelen, beide voor de productie van duurzame (beton gerelateerde) bouwmaterialen.

Mijn dank gaat in het bijzonder uit naar Prof. H.J.H. (Jos) Brouwers, promotor van mijn thesis, die mij het vertrouwen en de ruimte heeft gegeven om dit te kunnen voltooien. Onze samenwerking ervaar ik als zeer prettig en Jos heeft mij veel inzicht en ervaring meegegeven met betrekking tot het toepassen van secundaire mineralen en het interdisciplinair denken en onderzoek doen.

I thank my co-promoters Prof. Harald Justnes (Norwegian University of Technology) and Dr. Qingliang Yu (Eindhoven University of Technology) for their guidance, personal touch and pleasant discussions about detailed physical and chemical mechanisms. Verder gaat mijn bijzondere dank uit naar Andre van Zomeren (ECN) gezien zijn begeleiding m.b.t. de opzet en de structuur van specifiek uitlogingsonderzoek. Ook dank ik Peter Kakebeeke (Cementbouw), Dirk-Jan Simons (LBPSIGHT) en Steffen Grünewald (CRH) die altijd klaar stonden om mij te ondersteunen tijdens het onderzoek. Peter, door jouw manier van denken, interpreteren en inventieve manier van proefopstellingen bedenken, heb je mij op verschillende manieren naar onderzoek en chemische mechanismen leren kijken. Hierdoor waren resultaten veelal beter te verklaren, wat stimulerend werkte om verder in de materie te duiken. Dit is echt wat ik nodig had om het geloof en verbeelding in mijn onderzoek te behouden en wat zorgde voor een continue en positieve uitdaging. Ofwel volgens Albert Einstein: *'Logica brengt je van A naar B. Verbeelding brengt je overal'*.

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Geniet van het leven en blijf jezelf uitdagen.

Arno Keulen

Utrecht, februari 2018

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CHAPTER 1

Introduction

1.1 Background

The modern cements and concrete production is mainly based on primary (mineral) sources, i.e. Portland cement clinker, natural sand and gravel, at which their production has a significant impact on the natural and societal environment. However, Portland cement (PC) is the world's most used binder for the production of building materials. Portland cement (PC) is the world's most used binder for the production of construction materials. Due to its good mechanical property, relatively low cost, good durability and availability of the raw materials, PC concrete is favored in many applications. Nevertheless, the production of PC and natural aggregates for concrete production has some major drawbacks, e.g. depletion of natural habitat and fossil fuels, and high emissions of CO_2 and other greenhouse gas [1]. This leads to growing interests for searching alternative materials that can function as binder and aggregate material, by for instance applying industrial by-products as a partial precursor material instead of a primary raw mineral binder such as PC.

Billions of metric tons of waste and by-products e.g. slags and ashes (also named secondary alkaline minerals) are produced globally annually, by industrial thermal processes such as steel production, coal-fired power generation and municipal solid waste incineration (MSWI) [2]. These secondary alkaline minerals [3] and alkali activated binders [4] are widely discussed and promoted as potential materials for the production and development of more sustainable and functional cement concrete-based building materials. Besides, landfilling of these materials is increasingly banned within many European Union (EU) member states, instead the EU is promoting a circular economy for mineral waste and by-products. Therefore, potential secondary minerals are promoted to be re-used or recycled and subsequently applied in traditional or new processes or applications. In relation to this strategy, the EU Construction Products Regulation (CPR 305/2011/EU) has come into force. This EU regulation attempts to obtain more knowledge and junction, creating a generic and high level playing field between EU member states in regard to the re-use of mineral waste or by-products (related to environmental quality). The Netherlands is already strongly facilitating the re-use of many types of secondary materials in construction sector by a clear and workable regulation regarding the application and 'environmental quality' of building materials, described within the Dutch Soil Quality Decree [5].

In this thesis, the applied secondary minerals specifically refer to ground granulated blast furnace slag (GGBS), pulverized coal fly ash (PCFA) and MSWI bottom ash; and the alkali activated binder refers to alkali activated GGBS-PCFA binder in combination with sodium hydroxide and silicates activators. The key factors of the potential and the usage of these secondary minerals as well alkali activated GGBS-PCFA binders are likely to be determined by national and international (i.e. European Union) decision makers and

supporting players of the value chain. Through the implementation of new regulations and standards [6] and the development of new strategies (e.g. mineral circularity [7]) and products, these materials could become, in the near future, a commodity for cementbased building material production. Nowadays secondary minerals are increasingly used in Portland cement based concrete as a replacement of Portland cement, generally called supplementary cementitious materials or as aggregate to replace primary sand and gravel fractions [8,9]. However, due to their worldwide availability in combination with their potential pozzolanic or hydraulic material properties, secondary minerals are also of great interest within the development of alkali activated GGBS-PCFA binders. The literature increasingly recognizes the potential of alkali activated binders for the production of concrete with improved material durability properties, as well as to adapt towards the development of functional and sustainable building materials [4,10].

Designing alkali activated materials (AAM) for concrete with high durability largely depends on the mixture (precursor/binder) composition, mainly controlled by the GGBS and PCFA binder content and the concentration and type of alkaline activator(s). More specifically, a higher GGBS content as a replacement of the PCFA in the binder favors the matrix densification and the material strength development [11-14] by forming mainly calcium dominated gel-structures (C-A-S-H), consequently resulting in increased durability performance such as a reduced chloride migration rate in concrete [15]. However, to support the practical application and further development of alkali activated cements as well as that of Portland cements, both binder systems and related concrete production are strongly dependent on the availability and the effectiveness of plasticizing admixtures [16,17]. Overall, limited experimental studies have been performed on the effects of admixtures within AAM systems. Up to now, mainly the traditional Portland cement related admixtures has been tested. Often these admixtures are not able to sufficiently improve the fresh and hardened AAM concrete properties [18,19]. Nevertheless, polycarboxylate as well as naphthalene type admixtures, both having chemical structures which are less sensitive to hydroxide hydrolysis, has shown certain improvement within AAM. Summarizing relevant literature describing the observed effects of admixtures within AAM, the following observations can be drawn:

- Admixtures mainly enhance the AAM mixture workability over a short period of time (≤ 10-40 min) and an increasing GGBS and silicate activator content strongly reduce the workability, therefore AAM is often prone to a non-predictable, very rapid decline of the workability and fast setting [19–24].
- Admixtures frequently cause negative effects on the setting time and mechanical strength development of AAM [19–27].
- Admixtures can have either negative or positive effects on the concrete shrinkage [19,26].

Therefore further research is required in order to improve the physical/chemical understanding of the working mechanisms, as well as performance and predictability of admixture with AAM.

Apart from their filler (aggregate) or binder function, secondary minerals could contain variable amounts of potentially toxic metals and therefore specific attention should be addressed to their leaching behavior [28]. Alkaline minerals (slags and ashes) generally have a relatively high release of oxyanion metals (i.e. arsenic, vanadium, molybdenum, selenium, antimony and molybdenum) in comparison to primary minerals such as natural gravel and Portland cement clinker. For instance, oxyanion metals are mainly condensed at the outer fly ash particle surface, increasing their solubility potential [29,30], particularly in a (highly) alkaline environment (i.e. as in AAM and PC systems). In addition, the metal leaching behavior is mainly pH dependent and controlled by abundance of crystalline and amorphous phases, at which their abundance is directly related to the cement binder composition (mineral components) [28,31-35]. Overall, this leaching behavior of mainly oxyanionic metals should be fundamentally researched and understood in depth, as this could influence to the environmental quality (leaching) of the monolithic state concrete products. As well as the quality of the granular state aggregate materials which are produced at the end of the concrete's service life (concrete recycling) in a second life phase.

This research is performed to gain a deeper physical/chemical understanding of the technical and 'environmental' material properties and performance of secondary minerals, serving as binder source within alkali activated binder and as an aggregate source within Portland cement based concrete mixtures. In addition, more knowledge on the working mechanisms, effect of admixture in combination with alkali activated binders to produce modified alkali activated concrete materials is required, to adapt on an increasing demand of secondary minerals within the practice, for the production of more sustainable building materials.

1.2 Research objectives and strategy

Research objective

This thesis provides experimental and fundamental research on some of the major issues discussed in the introduction: (I) the technical and 'environmental' performance of secondary minerals (GGBS, PCFA and MSWI bottom ash) in different cement-based systems and (II) the physical/chemical performance of a polycarboxylate admixture in alkali activated binder system. Here "cement-based systems" is referred to alkali activated GGBS-PCFA cement and Slag cement (CEM III). The main objectives of this study are to provide detailed understanding in physical/chemical working mechanisms, the influence and effect of secondary minerals and admixture usage, as to optimize

cement-based mixture designs. To address these aims, the following objectives can be distinguished:

- To investigate the influence of a polycarboxylate admixture to modify the rheology of alkali activated GGBS-PCFA systems (tested in suspension, paste, mortar and concrete mixtures) and the identification of the physical/chemical mechanisms and effects of admixture on the AAM material development, microstructure and related concrete durability performance.
- To analyze the physical material properties and leaching behavior (metals and salts) of secondary minerals (slags and ashes and before and after treatment), as binder or aggregate resource for cement-based mixtures. As well as to analyze the leaching behavior and mechanisms (metals and salts) of monolithic (concrete) and granular (aggregate) material states of both alkali activated GGBS-PCFA and Slag cement (CEM III) mixtures, applying secondary minerals as binder or aggregates resource.
- To model the pH-dependent leaching behavior of elements (metals and salts) of single secondary minerals (slags or fly ashes, before and after treatment), as well as that of granular state materials, i.e. as aggregates, in the second life phase when the concrete product has been recycled. To predict the potential leaching of future aggregate under the influence of carbonation.

Strategy

This thesis comprises 5 sub-studies and they are presented in the 5 main chapters. The main research topics are related to determination of the technical and 'environmental' performance and related physical/chemical properties of the tested materials and applied binder systems:

- The material technical performances were addressed based on fundamental studies, which primarily focused on an alkali activated GGBS-PCFA binder system in combination with a polycarboxylate admixture to optimize the fresh and hardened mixture states. Furthermore, experimental studies were performed on bottom ash from a MSWI plant. The bottom ash was treated and characterized; the technical and 'environmental' performance as aggregate fraction was determined to replace natural aggregates in Slag cement-based concrete mixtures.
- The material 'environmental' performances were investigated by both experimental and modeling studies, which mainly focused on the leaching behavior and mechanisms or single secondary minerals (GGBS and fly ashes and MSWI bottom ash fractions before and after treatment). The leaching behavior and mechanisms of monolithic (concrete) and granular (aggregate) state materials, at which the secondary minerals (slags and fly ashes) are applied as binder or aggregate source in various AAM and Slag cement mixture designs were addressed.

1.3 Outline

The research outline is shown in Figure 1. In Chapter 1 the background, the objectives and the strategy of this thesis are described. Chapter 2 describes a fundamental research on the working mechanisms of a polycarboxylate admixture in alkali activated GGBS-PCFA blends. To gain an improved understanding of its physical/chemical mechanisms which influence the fresh and hardened material states. It appears that the admixture interaction with mainly calcium species strongly influences both the mixture rheology and related matrix and material strength development over time. In Chapter 3, the admixture performance is tested within AAM concrete production and the relations between the pore structure alteration, compressive strength and chloride migration over time that are changed by the admixture content are evaluated. It is found that the admixture enhances the rheological properties and the hardened state performance of AAM which are very beneficial for the practical application of AAM concrete and its durability performance. In Chapter 4, all the obtained knowledge of previous chapters is applied as it describes the design and performance of a unique building material, an ultra-lightweight alkali activated concrete. Relations between various mixture design approaches (in combination with admixture), to optimize the fresh mixture properties and hardened concrete performance are evaluated. Specifically, the use of highly porous expanded glass ultra-lightweight aggregates (produced from recycled glass) in combination with an alkali activated GGBS-PCFA binder showed promising results; a very low thermal conductivity and very low material density were obtained, while the compressive strength still was sufficiently high. In Chapter 5, the 'environmental' quality of alkali activated GGBS-PCFA mortars and concretes was analyzed, to determine the influence of various mixture parameters (activator concentration, GGBS-PCFA binder composition, liquid to solid ratio, curing time and compressive strength) on element (salts and metals) leaching. Specifically, the leaching of high mobile oxyanion metal species (As, Se, V, Mo and Cr) from monolithic and granular state samples was assessed. It was found through pH-dependent modeling that the GGBS-PCFA binder composition and system activator concentration and related material pH strongly determine the leaching and adsorption behavior of oxyanion metals within AAM.

Chapter 6 describes a comprehensive research of the treatment, characterization, application and performance MSWI bottom ash as secondary aggregates as a replacement of natural coarse aggregates in earth-moist concrete mixtures. This study is performed on large scale and under real life conditions, as bottom ash aggregates were produced in a pilot experiment which combined specially designed dry and wet treatment processes. Concrete mixtures were produced, containing treated bottom ash aggregates at replacement levels of 0-100 wt.%, which were tested with regard to environmental (element leaching) and mechanical performance. It is shown that bottom ash aggregates have a comparable to even improved performance in relation to natural aggregates.

Finally, Chapter 7 describes the main results of this thesis and conclusions are drawn, and recommendations are given for the engineering practice and for future research.



Figure 1: Outline of this thesis.

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CHAPTER 2

Working mechanism of a polycarboxylate superplasticizer in alkali-activated slag-fly ash blends*

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ADMIXTURE EFFECT TO ENHANCE PARTICLE DISPERSION AND MICROSTRUCTURE DEVELOPMENT



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Abstract

This chapter investigates the working mechanism of a polycarboxylate plasticizing admixture in alkaline activated slag-fly ash blends, by examining the fresh state behavior and hardened material properties over time. To provide more understanding of admixture use in terms of its physical/ chemical (complexation and/or adsorption) working mechanisms in an alkaline activated slag/ fly ash blends.

The liquid demand of slag and fly ash decreases up to 25% and both minerals become significantly more sensitive to additional liquid when the admixture is applied. The admixture significantly improves mixture rheology, at the dosage of 0.2 wt.% of the binder the mortar slump flow increases up to 52%, and a linear relationship is obtained between slump flow and admixture dosage. The admixture strongly favors the 'ligand' formation and adsorption behavior of mainly calcium ion species. Consequently, an increased calcium complexation favors the inhibition of the early age microstructure development, while further over time, the mortar strength significantly increases. At 28 days, a compressive strength of 47 MPa is achieved using the admixture compared to 31 MPa of the reference mixture. This strength improvement coincides with the presence of a thicker amorphous gel layer around the GGBS particles, 34% compared with a non-admixture containing reference.

Keywords: rheology; admixture; element leaching; compressive strength;

1 Introduction

The rheological behavior of alkali-activated concrete mixtures can be affected by various parameters such as the liquid to binder ratio (L/B), activator type and concentration [1– 4], type and properties of the precursors (e.g. particle size, shape, chemical composition and reactivity) [1,5,6]. However, gaining a highly effective, stable and predictable workability of an AAM mixture, limited effectiveness has been obtained by admixture use [7-9]. Nevertheless, polycarboxylate as well as naphthalene type plasticizing admixtures have shown potential in ground granulated blast furnace slag (GGBS) and (pulverized coal fly ash) PCFA alkali-activated materials. Both are possibly less sensitive to hydroxide hydrolysis of the initial admixture molecular structure while they have a clear effect on enhancing the workability of alkali activated PCFA blends [5,8,10], and to a lesser extent on alkali activated GGBS blends [8,9,11–13]. It's reported that these polymer types are able to significantly reduce the liquid demand and related liquid to binder ratio of AAM mixtures [7] and to enhance the mixture rheology parameters over a 'relatively short' period ($\leq 10-40$ min). However, admixture performance significantly declines at an increasing (reactive) GGBS binder content and a higher liquid silicate activator dosage, which in both cases strongly reduce the workability and subsequently lead towards fast setting [5,7,8,11,12,14].

Within the group of polycarboxylate type admixtures, a broad variety of products is available, although their chemical (molecular) structure is of large influence on the adsorption and complexation reaction mechanisms [13,15]. Research on Portland cement based materials has observed the following working mechanisms, which affect the mixture rheology: (I) Admixture is adsorbed onto (cationic charged) binder particle surface, mainly by calcium bridging, associated with the negatively charged reactive side chain groups (i.e. carboxylic). This results in steric forces, keeping particles at distance by the chain length of the molecule structure, promoting flowability [16–20]. (II) Admixture is adsorbed onto the particle surface and changes the local charge of the particles surface, initiating a change of the electrostatic force which leads towards more repulsive forces between colloids avoiding particle agglomeration [18,21].

These polycarboxylate related mechanisms have not yet been fully understood although it is widely accepted that the amount, composition and length of the reactive side chain groups, abundant on the molecular backbone, play an essential role [13,22–24]. A higher admixture complexation potential favored by more reactive groups, mainly with calcium, by forming ligands is of great importance concerning its working mechanisms. This calcium complexation potential could significantly influence the microstructure development over time. It has been reported that this complexation behavior can disturb the ion dissolution of mineral binder and related ion (gel) nucleation processes [15,25]. Therefore, its utilization on enhancing the AAM mixture rheology could have negative side-effects, for example retarding the early and later age mechanical strength development and other related material performances (i.e. shrinkage) [4,5,7,8,10–12,14,25,26].

However, some researchers reported that its use could result in positive side-effects, resulting densified microstructure development by creating a reaction product layer around aggregate and precursor particles, which improves the AAM material strength [27]. Despite their widespread utilization in Portland cement based materials, these admixtures are currently still the subject of AAM studies. Most published studies mainly focus on the physical material performance, e.g. rheology (fresh state) and mechanical strength (hardened state) effects by admixture. Limited researches have addressed the working mechanism (e.g. adsorption, complexation etc.) of a plasticizing admixture in AAM system.

This study aims to address the physical/chemical mechanisms of a polycarboxylate based plasticizing admixture in alkali-activated GGBS-PCFA system. The element concentration, liquid demand, zeta potential and slump flow of AAM in fresh state and microstructure development overtime are investigated:

- 1) Alkaline GGBS and PCFA solutions with different admixture dosages were tested on ion complexation behavior, by analyzing the calcium, aluminum and silicon concentration.
- 2) The rheological properties of alkaline activated GGBS and PCFA pastes were tested and the effects of admixture on the liquid demands were evaluated. Additionally, the rheology properties of alkali activated GGBS-PCFA binder, depending on the admixture dosage were analyzed over time by zeta potential measurements.
- 3) The microstructure development of paste and mortar over time was analyzed.

2 Materials

The applied liquid polycarboxylate admixture, termed 'admixture', is supplied by SQAPE Technology (The Netherlands). The admixture is highly soluble in water and the backbone contains poly-functional reactive side chains, mainly carboxylic groups. The following precursors were used; class F type pulverized coal fly ash (PCFA) according to NEN-EN 450 and ground granulated blast-furnace slag (GGBS). Both materials were blended to produce a mineral blended binder (MB), composed of 73.67 wt.% PCFA, 25 wt.% GGBS and 1.33 wt.% (99% pure) meta-silicate powder. The chemical compositions of both precursors and the mineral blended binder are determined by X-ray fluorescence (XRF), shown in Table 2.1
Oxides	PCFA	GGBS	MB	
SiO ₂	59.7	34.3	51.4	
Al ₂ O ₃	24.6	9.8	17.9	
CaO	1.5	41.8	13.9	
Fe ₂ O ₃	6.8	0.5	6.3	
MgO	1.3	7.7	3.8	
K ₂ O	3.0	0.6	2.2	
Na ₂ O	0.6	< 0.1	1.1	
TiO ₂	1.2	1.2	1.1	
Mn ₃ O ₄	0.0	0.3	0.2	
BaO	0.1	0.1	0.1	
P_2O_5	0.1	<0.1	0.4	
SO ₃	1.0	3.6	1.7	
Cl	< 0.1	<0.1	< 0.1	
LOI (950 °C)	0.9		1.6	

Table 2.1: Elemental composition (%) of the mineral blended binder (MB), determined with XRF.

LOI: loss of ignition

The low silicate powder addition, as a part of the MB, is applied to increases the material strength at the early ages of 1 day to 7 days, while higher silicate dosages (> 1.3 wt.%) would reduce the mixture workability. A commercial sodium hydroxide (NaOH), with the concentration of 33% (molarity (M) of 11.2), was diluted by tap water to obtain the desired system alkalinity (3M NaOH in the present study). According to the literature [29–31], alkali-activated GGBS-PCFA mortars with a concentration \geq 3 M NaOH is sufficient for an effective alkali activation reaction. At this alkalinity level, the initiation of effective element dissolution and related gel condensation mechanisms of mainly GGBS particles is obtained. For all mixtures, the sum of water, NaOH and admixture were considered as the liquid content. For mortar mixtures, oven dried (24 h. at 80°C) natural 0-4 mm sand was applied. Relevant material properties are listed in Table 2.2.

Table 2.2: Material properties.

Material	Specific density (kg/m ³)	Blaine value (cm²/g)	d ₅₀ (μm)
PCFA	2334	2700	24
GGBS	2893	4200	12
Mineral binder (MB)	2498	3100	15
Sand 0-4 mm	2611		
NaOH solution (33%)	1360		
Admixture	1190		

3 Experimental methods

3.1 Solutions: Zeta potential and element concentration

Zeta potential measurements were carried out to analyze the change in electrostatic charge between binder particles, using a Malvern Zetasizer (nano-series) with demineralized water as the carrier liquid. Solutions were prepared and differed in: (I) admixture contents (0 to 6 ml within 200 ml total liquid volume) and (II) mixing time (0 to 60 min.) with a fixed admixture content (6 ml). The applied mineral blended binder (MB) (75 wt.% PCFA and 25 wt.% GGBS) does not contain sodium silicate powder, as this material may disrupt the measurement. Dry MB binder (200 g) was mixed with 200 ml (including admixture) of 3M NaOH liquid (L/S of 1), using a high speed mixer (7000 RPM). After 10 min of mixing, a sample of 10 ml was extracted (high speed mixer on 5000 RPM to maintain stirring) which was diluted in 990 ml demineralized water. This 1-liter specimen is toppled over in a graduated cylinder to settle the large size unwanted particles. During the settling the pH of the liquid was measured over time. After 10 min. about 5 ml liquid is extracted (with a plastic syringe) from the top of the cylinder (top layer contains the smallest particles that settle more slowly). The extracted liquid was filtrated by a 1 µm glass filter and transferred to the Zetasizer electrode for analysis. Furthermore, batch leaching tests were performed to analyze the element concentration (complexation), primarily calcium, aluminum and silicon, in alkali activated solution (sole PCFA or GGBS) in order to evaluate the adsorption potential of the admixture. Solutions were prepared and differed in admixture content (0 to 4 ml admixture in 200 ml liquid). These leaching tests were performed in accordance with NEN-EN 12457-3 "compliance test for granular samples". Dry PCFA or GGBS (40 g) was mixed with 200 ml (including admixture dosage) of 3M NaOH liquid, with a liquid to solid (L/S) ratio of 5. A low L/S of 5 was used instead of the standard L/S of 10 set by NEN-EN 12457-3 in order to generate higher concentrations that can be more reliably determined. The

solutions were shaken for 24 h before filtration over 0.45 μ m paper filter. In total 40 ml eluate was acidified with 9 ml 70 % pure nitric acid, to a pH \leq 2. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used for elemental analysis.

3.2 Pastes: Water demand

The water demand of the sole precursor (PCFA or GGBS) was determined by using paste samples. Two mixture scenarios were analyzed, which varied in liquid compositions: (I) within a neutral (water) and highly alkaline (3 M NaOH) solution and (II) in a highly alkaline (3 M NaOH) solution in combination with a fixed admixture content. The applied admixture dosage (8 ml) is calculated as an average quantity, in relation with the slump flow analysis dependent on the admixture content of mortar mixture (Table 2.4). Where the average admixture dosage is ≈ 3 ml admixture on 450 gram of binder within a total ≈ 870 ml mortar volume). For the liquid demand experiments, the method described in the literature [32] is followed, using a Hägermann min-cone (100 mm base diameter, 70 mm top diameter and height 70 mm). Firstly, dry material (1 kg) is mixed together with an initial liquid volume, to gain a low paste small spread flow. It should be noted that within this first mixing step, the total admixture content (8 ml) was added as a part the liquid volume. The initial and added liquid quantities applied within the experiments are listed in Table 2.3. Secondly, liquid quantities in the test mixtures were increased stepwise (total of 4 additions with the same interval) and at each mixing step the spread flow was measured.

Material-liquid	Start volume (ml)	End volume (ml)	Liquid steps (ml)
PCFA-water	430	490	20
PCFA-NaOH	420	480	20
PCFA-NaOH-Ad	325	385	20
GGBS-water	330	390	20
GGBS-NaOH	310	370	20
GGBS-NaOH-Ad	265	295	10

Table 2.3: Total liquid quantities and steps used with the GGBS and PCFA $(\beta_{\textrm{p}})$ liquid demand experiments.

Ad is the abbreviation of admixture.

3.3 Mortars: slump flow and compressive strength

Mortars were composed to analyze the fresh state (slump flow) and hardened state (compressive strength) properties, listed in Table 2.4. The sample preparation follows NEN-EN 197-1 as a reference. The tested mixture A1 till A6 have a higher L/B ratio (0.38), to initiate an enhanced fresh mixture workability, affected by the admixture. Mixture B1 till B6 (L/B of 0.31) were designed to evaluate the compressive strength

development. During the mortar preparation, all components (binder, sand, 3 M NaOH and admixture) were mixed at once with a Hobart mixer for 3 min at a medium speed. Fresh mortar mixtures, with a total volume of ≈ 870 ml per mortar composition, were analyzed on mini slump flow with a Hägermann mini-cone, in accordance with EN 459-2. Then the mortars were cast in polystyrene prism molds ($40 \times 40 \times 160$ mm³), levelled on a compaction table, sealed with plastic foil to prevent moisture evaporation and stored for curing in a climate room ($20 \ ^{\circ}C$ and $\geq 95\%$ RH) until compressive strength testing, in accordance with NEN-EN 196-1.

Mixture	Sand (g)	MB (g)	Total liquid (ml)	L/B ratio	NaOH (M)	Admixture (ml)
A1-A6	1350	450	<u>170</u>	0.38	3	0/1/2/3/4/5
B1-B6	1350	450	<u>140</u>	0.31	3	0/1/2/3/4/5

Table 2.4: Mortar mixture compositions.

All the varied parameters per series are bold and underlined.

4 Results and discussions

4.1 Effect of admixture on the ion concentration in solution

The literature states that polycarboxylate-based admixture can interact with mainly cationic species in alkaline solutions to form metal complexes. At which through hydrolysis mechanism of the initial admixture molecule, initiated by the high alkalinity, the number of free reactive (carboxylic) groups is increased. At which the admixture gains a higher charge density and an improved adsorption ability, which could interfere element dissolution and nucleation and reaction mechanisms within an AAM system [23,25]. Figure 2.1 show the calcium, aluminum and silicon concentrations of sole PCFA and GGBS in a 3 M NaOH alkaline solution (sample pH >14), dependent on the admixture content. It should be mentioned that in total 26 elements were measured, while only Ca, Si and Al are shown because of their dominant role in the composition of the AAM microstructure, in addition to oxygen (O) and hydrogen (H).



Figure 2.1: (a) calcium, (b) silicon and (c) aluminum concentrations of GGBS and PCFA versus admixtures content.

The Ca concentration (Figure 2.1a) and related trend lines displayed by both GGBS and PCFA, imply a direct correlation between the admixture content and Ca concentration. In addition, GGBS shows much higher concentrations at the same admixture content in comparison with PCFA. This can be explained by the much higher reactivity and richness in Ca of GGBS, which favors admixture adsorption (metal complexes) [28,33,34]. It is noteworthy to observe the very large Ca concentration difference between the reference sample (0 ml admixture) with 35 and 62 mg/kg dry matter (dm) for PCFA and GGBS, respectively, in contrast with the admixture containing samples with show Ca concentrations with a factor 100 times higher. Additionally, Figure 2.1

shows that the Ca concentration (cationic metal) increases, due to metal complexation when applying the admixture. This results in a retardation of its nucleation reaction and consequently results in the significant increase of free cationic ion concentrations [28,38]. This effects of cationic metal complex formation is further confirmed by the measured increased amount of magnesium (Mg) and iron (Fe) species for both GGBS and PCFA, although their concentrations were much lower (data is not added). However, normally the Ca concentration dramatically decreases when increasing the pH of an alkaline solution [30,35], as rapid incorporation of Ca into calcium (sodium) silicatealuminate hydrate structures [30,34,36,37] and possibly temporarily precipitation as calcium hydroxide at pH >12.5 will occur. The adsorption and complexation with cationic species begin when applying the admixture, which retards nucleation reaction and consequently results in the significant increase of free cationic ion concentrations [28,38]. This effectof metal complex formation is further confirmed by the measured increased amount of magnesium (Mg) and iron (Fe) species for both GGBS and PCFA, although their concentrations were much lower (data is not added).

Figures 2.1b and 2.1c show that the Si and Al concentrations also increase at a higher admixture content which tends to follow a similar pattern to that of Ca. This difference in concentration level is attributed to the initial Si and Al morphological state and related dissolution mechanisms within PCFA and GGBS as aluminum form anionic species in solution, such as $Al(OH)_4^{-}$, and so does silicon, albeit less defined. It is often considered that silicon species may be composed of several silicate units (aluminosilicate), since they are tetrahedrally coordinated with oxygen [37,39]. In this way both Si and Al species do not, or less favorably, form admixtures complexes. However, dissolved Si and Al species are electrostatically connected as negative charge balancer to the admixturecalcium complex, creating an equilibrium (mechanisms are illustrated in Figure 2.1). It is noteworthy that the Si and Al concentrations in the reference samples are much higher than those of samples that contain admixture, which is opposite in comparison with Ca. This can be explained by the alkaline dissolution of the PCFA and GGBS surface that are mainly chemically composed of glassy silicates and aluminates. This leads to high concentrations of dissolved sodium silicate-aluminate species. However, within the mixtures that contain admixture, Si and Al concentrations are increased with the increase of the admixture content, which confirms that admixture favors elements complexation and adsorption reaction mechanisms.

The data plotted in Figure 2.2 show linear correlation between the concentrations of Ca and Si, Ca and Al and Si and Al. A higher admixture content results in a higher calcium absorption potential for both GGBS and PCFA, supported by a higher concentration of Si and Al, or aluminosilicate species. As both anionic species predominantly act as negative charge balancer, within the admixture related carboxylic-calcium complex.



Figure 2.2: Correlation between (a) calcium and silicon, (b) calcium and aluminum (c) silicon and aluminum concentrations of GGBS and PCFA related to the admixtures content (1 till 4 ml).

In overall, the observed behavior of Ca concentration affected by admixture could be of significance on the zeta potential, which will be analyzed in Section 4.3. As reported in [40,41], a change in zeta potential in an alkaline system applying GGBS as the precursor is related to the ion and particle adsorption of the admixture at which calcium is of great importance [42].

4.2 Effect of admixture on the liquid demand of PCFA and GGBS

The rheology modification properties of the admixture were analyzed by liquid demand (β_p) experiments. Figure 2.3 shows the differences in liquid demand of sole PCFA and GGBS dependent on the liquid compositions (neutral to alkaline conditions), with or without admixture. Relevant results of the water demand experiments are summarized in Table 2.5. In comparison with only water, introducing NaOH in the paste system enables a slightly (4 %) lower liquid demand for both PCFA and GGBS. However, combining NaOH and admixture, a significant decline of liquid demand for both precursors initiated by the admixture is observed. Additionally, for GGBS the decrease of the liquid demand of 25% is slightly larger than that of PCFA with 21%. On average PCFA shows an overall 40% (factor \approx 2) lower liquid demand than GGBS. This observation is also in line with Portland cement (PC), where normally PCFA enables a much lower liquid demand than GGBS and PC.



Figure 2.3: Liquid demand of GGBS and PCFA using different liquids composition.

From the slope of the linear water demand curve, the deformation coefficients (E_p) is calculated (see Table 2.5) which, explains the deformability changes (sensitivity) of the precursor to a certain liquid dosage and the influence of liquid variations on the relative slump [32]. In line with the liquid demand, PCFA is two times more sensitive to change its flowability in comparison with GGBS in both water and high alkaline solution conditions. Additionally, the deformation sensitivity for both minerals significantly increases under alkaline condition when admixture is used. This observed admixture effect on the precursor liquid demand and modified rheology behavior can be further

explained by the zeta potential analysis which will be presented in Section 4.3 and the mortar mixture slump flow performance analyzed in Section 4.4.

Material-liquid	R ²	β _p	E _p	β_p related to water reference	E _p related to water reference	
PCFA-water	0.997	0.754	0.027	100%	100%	
PCFA-NaOH	0.999	0.723	0.027	96%	100%	
PCFA-NaOH-ad	0.918	0.594	0.010	79%	37%	
GGBS-water	0.984	1.303	0.054	100%	100%	
GGBS-NaOH	0.992	1.252	0.055	96%	102%	
GGBS-NaOH-ad	0.989	0.979	0.023	75%	43%	

Table 2.5: Water demand properties of PCFA and GGBS within various liquids compositions (water, 3 M NaOH with and without admixture).

 R^2 : linear correlation, β_p : liquid demand related (Volume of Water/ Volume of Powder), E_p : related deformation coefficient of βp linear result. Ad: admixture.

4.3 Effect of admixture on the Zeta potential

In order to evaluate the electrostatic forces interaction between particles in an AAM system under the influence of admixture adsorption, zeta-potential (ζ -potential) measurements were performed. Figure 2.4 shows the ζ -potential of blended PCFA and GGBS (75 wt.% : 25 wt.%) in alkaline (NaOH) solution, versus admixture dosage and reaction time, respectively. It should be noted that all tested solutions have an equal pH of 12.2, to eliminate the pH influences on zeta potential change [2,40]. Furthermore, the research on Portland cements and GGBS in different electrolyte solutions reveals that Ca and chlorine are potentially zeta potential determining ions, whereas sodium (Na) shows no influence [40]. This favors the identification of the admixture behavior on particles in Na-based alkaline systems, without having a potential Na-ion disturbance.



Figure 2.4: (a) Zetapotential versus admiture content (b) zetapotential versus mixing time under a fixed high (6 ml) admixture content.

Figure 2.4a shows that the ζ-potential firstly slightly increased when increasing the admixture dosage within the solution from 1.5 ml to 2.5 ml and then decreased quickly when further increasing the admixture dosage. This behavior is in line with the reported (polycarboxylate) admixture adsorption/complexation mechanisms in both Portland cement [18,28,43] and alkali active GGBS system [33,34,44]. In addition, the observed zeta potential behavior (Figure 2.4a) can be explained by the element leaching experiments (Section 4.1). A larger zeta-potential is obtained because more admixture is adsorbed onto the particle surface, at a higher admixture content (Figure 2.4a), due to the interaction between its negative charged reactive carboxylic group with the positively charged cationic (mainly calcium) sites of the binder particles [28]. Overall, the larger negative zeta potential resulted from the higher admixture content is attributed to more repulsive forces between particles, thereby improving the mixture stability [43] that can enhance the mixture fluidity. Figure 2.4b shows that the zeta potential is significantly affected by admixture reaction time. Firstly, ζ-potential becomes more negative up till about 40 min mixing time, where lower negative charges indicate more repulsive forces between particles, avoiding agglomeration and improving the mixture rheology [20,45].

Then, from 40 min till 50 min mixing time, the ζ -potential stabilizes and then becomes less negative when further increasing the mixing time to 60 min., indicating a decline of the inter-particle repulsive forces and the initiation of particle agglomeration and thereby a reduction of the paste flowability and slump flow loss of the mortar mixture [43]. The influence of both system parameters, admixture dosage and reaction time, are further analyzed in the mortar slump flow experiments, which will be discussed in Section 4.4. Overall, the investigated admixture related zeta potential results (\geq 15-30 to 50 mV) indicate a moderate to good mixture stability [42].

4.4 Effect of admixture on the mortar workability

Figure 2.5 shows the mini slump flow of mortars as a function of the admixture content (0 to 5 ml), having a fixed 3M NaOH alkalinity and mineral binder (MB) composition (mixtures A1-A6, described in Table 2.4).



Figure 2.5: Slump flow of fresh mortars mixtures A1-A6 over time (mortar volume≈ 870 ml). R2: qaulity of liniear trend of the data point between 0 till 5 ml admixture. T: as a function of time (minutes).

The critical dosage is about 1 ml, at which the onset of flow is initiated. Further increasing the admixture content results in further increase of the mixture slump flow. This is supported by the zeta potential results (Figure 2.4a), as more repulsive forces between particles are initiated as an effect of a higher admixture content. A noticeable admixturerelated effect was observed on the slump flow behavior over time between 5 and 20 min and especially when a higher admixture content is applied (≥ 2 till 5 ml). Within this period the slump flow is further improved, afterword's it starts to steadily decline. It is proposed that this slump flow enhancement (between 5-20 min.) is attributed to the hydroxide hydrolysis of the initial admixture molecular structure. Theoretically, this may cause a change of the steric molecular structure or poly-dispersion (amount, size and length), which enhances the fluidity [20]. The downwards parabolic slump flow pattern of mortar mixtures is in line with the observed upwards parabolic zeta potential pattern (Figure 2.4b). Firstly, the initial slump flow after 5 min significantly increased, which relates to the increase of the negative zeta potential value. Secondly, mortar fluidity declines between about 20 to 60 min, which relates to a stabilization and decease of the negative zeta potential value. However, in the zeta potential experiment the change towards a more negative zeta potential was observed slightly later, after about 25 min. of mixing, instead of the noticed second mortar slump flow enhancing peak at about 20 min after mixing. This can be possibly explained by the higher L/S ratio in the zeta potential experimental design, resulting in lower element concentrations and related slower reaction kinetics.

Further, the admixture was able to control the workability over time, showing a moderate steady decline of the slump. This is consistent with the previous research results, applying the same admixture in ultra-lightweight AAM concrete [46] and with the literature where polycarboxylate admixture is applied in Portland cement containing a high PCFA content [47]. At the admixture dosage of ≥ 2 to 5 ml, the mixture slump flow decline rate between 5 to 60 min is more reduced, implying an extended mixture setting time. This effect is also observed in AAM systems as well as Portland cement systems [7,8,12,19,47] at which an increasing admixture adsorption, as a function of a higher admixture content, onto the mineral precursor particle surfaces behavior is observed [18,19,23,41]. This connection keeps the particles electrostatically or sterically at distance, enhancing the mixture workability.

The error-bars shown in Figure 2.5 are obtained from duple performed experiments. Since PCFA is the dominant precursor, two different PCFA production batches were tested as binder precursor. Although both were produced at the same energy plant, they differ in material properties, as described in Table 2.6. The slump flow deviations can be originated to the total carbon content (TCC) of the ashes, as measured by loss of ignition (LOI). Batch-2 shows a 4 times higher LOI than Batch-1, resulting in an overall lower slump flow. Therefore, it is attributed that more admixture is absorbed by the porous carbon particles in PCFA-batch 2, which will decrease the flowability.

Material	LOI (950 °C) (wt.%)	Water demand (ml)
PCFA-batch 1	0.85	25
PCFA-batch 2	3.54	32

Table 2.6: Materia	l properties o	f two batches	PCFA.
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LOI: loss on ignition/ Water demand: determined conform NEN-EN 13179-2.

4.5 Effect of admixture on the mechanical property

Figure 2.6 shows the compressive strength development of mixtures having a fixed 3M NaOH alkalinity and mineral binder (MB) as a function of the admixture content (0 to 5 ml) (described in Table 2.4).



Figure 2.6: Compressive strength development of mortar mixtures B1-B6 versus admixture content (mortar volume≈ 870 ml).

It should be noted that the data demonstrates a very low deviation between each measurement as shown by the error bars (Figure 2.6). A higher admixture content results in a stronger inhibition of the early 1 to 7 days strength development, in comparison with the reference (mixture without admixture). This is supported by the significantly extended mortar setting, caused by a higher admixture content (described in Section 4.4). The admixture (polycarboxylate) related early age strength retardation effects on AAM systems are also reported in the literature [11,12,48,49]. Apart from these observations and limited physical/ chemical explanation within these studies, the possible interfering mechanisms to reduce the early age strength can be related to the admixture adsorption and complexation mechanisms [24,25] (further reported in Section 5.1). However, in the period between 7 and 28 days an opposite strength development effect is observed. Mortars with a higher admixture content (between 1 till 3 ml) generated higher strengths up to 48 MPa (mixture with 3 ml admixture). This is significantly higher (54%) compared to the reference mixture of 31 MPa. This admixture-strength behavior is in line with the previous research on AAM concrete production, on the dependence on the admixture content and this effect is further discussed in Section 5.2.

5 Discussions

5.1 Admixture adsorption and complexation mechanisms

Both the ion concentration analysis (Section 4.1) and the zeta potential analysis (Section 4.3) reveal a significant relation, of a high affinity between the admixture content and ion interaction in a alkaline system. These results allow to assume that the polycarboxylate admixture backbone structure which contains highly charged polyfunctional reactive (carboxylic) side chains groups, enables a high ion adsorption and complexation potential. Based on the obtained data and the improved physical and chemical understanding within the this study, the following admixture ion interaction mechanisms are likely to occur: (I) complexation with mainly with divalent cationic species such as calcium [28] and (II) adsorption due to calcium bridging onto the surface of the mineral binder precursors (GGBS and PCFA) [18]. These mechanisms are illustrated in Figure 2.7, showing the general admixture structure and the chemical interaction.



Adsorbtion (bridging) on to cationic solid precursor particle surface Figure 2.7: Chemical structure and adsorption mechanisms a carboxylic side chain group of polycarboxylate: carboxylic group (1) at the molecular admixture backbone, (2a) complexation of divalent cation (M⁺) in solution, mainly calcium by two carboxylic groups, (2b) complexation of divalent cation with a carboxylic groups and silicate and aluminate species (X) as charge balancer and (3) admixture adsorption onto particle outer surface due to calcium bridging with the carboxylic group.

R: backbone structure of admixture, C: carbon, O: oxygen, H: hydrogen.



5.2 Calcium complexation vs. retardation

It is shown in pervious sections and the literature [18,28,38] that polycarboxylates may interfere the dissolution mechanisms [24,25] of GGBS and PCFA (aluminosilicate precursors) in an alkaline environment [33,34]. This can result in inhibition or disrupting of nucleation or gel condensation growth and related early age strength development. To further understand the admixture interaction with calcium and its possible influence on the microstructure, the relation between the compressive strength of mortar mixtures containing different amount of admixture and the Ca concentration in the liquid phase is investigated. Figure 2.8 shows the relation between the compressive strength of mortar mixtures at the age of 24 hours and their Ca concentration in the liquid phase at 24 hours, affected by admixture dosage. It should be noted that the strength results are obtained from mixtures A1-A6, as described in Table 2.4. These mixtures have a higher L/B ratio than mixture B1-B6, which is more closely related to the measured calcium concertation, from the single GGBS and PCFA leaching experiments (L/S of 5) under the influence of the admixture content (data shown in Figure 2.1a). Calculations were based on the calcium concentration of single GGBS and PCFA with different admixture dosages, multiplied with the binder applied in the mortar (25 wt.% of GGBS and 75 wt.% of PCFA). The derived logarithmic trend (R^2 = 0.98) between the Ca concentration and compressive strength indicates that a higher admixture content favors a higher Ca concentration in the liquid phase within the first 24 hours, which in turn corresponds to lower of strength development. This calcium related phenomena has been observed in studies on dissolution reaction kinetics of supplementary cementitious materials [50], and in alkaline activated GGBS using polycarboxylate admixtures [33,34] that reported that too high Ca concentrations in solution towards a more saturated state cause a strong inhibition of the overall element reaction kinetics. This ultimately retards the gel condensation and microstructure development such as calcium aluminate silicate hydrate phases formation in a alkaline active GGBS system [33,34]. It can be concluded that admixture (polycarboxylate) use and its predominantly Ca adsorption ability [28] in alkali activated slag-fly ash systems disturb the fast dissolution of GGBS and precipitation of reaction products [30,36,37]. This results in retardation of early age (matrix) compressive strength development.



Figure 2.8: The 24 hour compressive strength of mortar versus the calculated calcium concentration of mineral binder in solution at 24 hour and. Data points in the figure represents the admixture dosage 0, 1,2,3 and 4 ml.

5.3 Admixture adsorption vs. microstructure development

From previous research [51], the microstructure analysis on pastes (with and without the admixture) at the age of 28 days was performed to identify the nature of the reaction products. These mixture compositions were based on the mortar mixture B1 (0 ml admixture reference) and B4 (3 ml admixture), as described in Table 2.4. The dominant gel structure (data obtained by X-ray energy dispersive (EDX)) is a C-A-S-H or a hybrid C-(N)-A-S-H type binding phase, although near the PCFA particles N-A-S-H or a hybrid N-(C)-A-S-H structures are also observed. These observations are in line with the literature [52,53] on comparable sodium hydroxide activated GGBS-PCFA systems. Figure 2.9 shows environmental scanning electron microscopy (ESEM) pictures of the paste matrix with and without admixture and their differences in gel layer thickness (reaction product) around the solid precursor particles. Size estimation of the reaction product layer was done using the Digital Micrograph 1.0 program.



Figure 2.9: Gel layer thickness (reaction product) on PCFA and GGBS particles of (a) non-admixture and (b) with admixture (3 ml) in paste samples at the age of 28 days.

The GGBS particles (red arrow) are overall light grey, rectangular shaped, while PCFA are darker grey, round shaped containing hollow spheres. The average reaction product layer around GGBS particles is about 1.50 μ m (standard deviation 0.13 μ m) without admixture (Fig 9a) and 2.25 μ m (standard deviation 0.17 μ m) with admixture (Fig 9b). However, further research should be done, to investigate the porosity of the admixture modified layer in comparison with that of the reference sample. For PCFA particles the modification was less prominent, which can be explained by the high abundance of mainly Si and Al reaction sites and heterogeneity of the chemical composition of the particles surface which thereby lowers the admixture interaction potential. To finalize the following mechanisms are proposed to explain the admixture modified gel layer: Firstly, (polycarboxylate) admixture is strongly adsorbed onto the particle outer surface of the mineral precursor due to cation bridging. This effect is stronger for GGBS due to its high Ca content and related particle (Ca) reaction sites, which as a result interfere or disturb the dissolution of precursors and gel nucleation mechanisms [24,25,28,41,38].

Secondly, the adsorbed admixture forms more complexes with cationic (calcium) species at its remaining active carboxylic groups, where the complexation capacity strongly depends on the number of free reactive groups (the molarity) [23]. This will attract silicate or aluminate species as negative charge balancer, which is in line with the observations in Section 4.1, showing a strong relation between Ca and the abundance of Si and Al species. This synthesis of inorganic-organic hybrid structures with the admixture as 'organic' part results in self-assembly (nucleation) of newly formed optimized gel oligomerization structures as precipitates around the precursor particles, thickening the reaction layer and strength performance of the material [25]. Further, this improved gel (reaction product) layer thickness could be related to the enhancement of the aggregate bond to the gel matrix, known as interfacial transition zone (ITZ). The literature shows that the addition of a plasticizing admixture in AAM systems modifies the ITZ [27], thereby enhancing the material strength performance. This can be supported by the significant compressive strength modification at 14 to 28 days caused by the higher admixture content (Figure 2.6).

6 Conclusions

This chapter investigates the effects of a plasticizing admixture (polycarboxylate type) on the fresh and hardened material state of an alkali activated GGBS-PCFA system. The admixture addition provides enhanced rheological properties due to adsorption and complexation mechanisms, and modifies the material microstructure development. The following conclusion can be drawn:

- Admixture adsorption and complexation with mainly cationic divalent ion species controls the calcium concentration in the liquid phase by forming ligands. This goes along with the increase of silicate and aluminate concentration, as both species act as negative charge balancer to the admixture (carboxylate)-calcium complexes.
- Admixture in an alkaline paste mixture reduces the liquid demand of GGBS and PCFA, by about 21-25%. The liquid demand of PCFA is approximately a factor of 2 lower than GGBS.
- Higher admixtures dosages result in higher repulsive (electrostatic) forces between particles affected by a more negative zeta-potential, gaining an enhanced mixture stability.
- Within the first period (up to 20 min) after initial mixing, the mixture rheology (mortar slump flow) and stability (zeta potential) is further slightly modified. This is attributed to the hydroxide induced hydrolysis of the initial admixture molecular structure, causing a change of the steric molecular structure or poly-dispersion (amount, size and length), enhancing the fluidity.

- A higher admixture dosage slows down the dissolution reaction of the precursor, mainly GGBS, due to its high adsorption capacity. Additionally, the admixture forms complexes with calcium in solution at which a higher Ca concentration, related by a higher admixtures content, results in a strong inhibition of the early age microstructure development and related compressive strength.
- The mortar compressive strength significantly develops at later age, at a higher admixture content. At 28 days the strength of admixture-containing mortar (optimum with 2-3 ml admixture) were about 44 to 48 MPa, while the reference concrete was 30 MPa. This is attributed to a significantly thicker reaction product layer, typically around GGBS particles as a result of admixture adsorption affected by calcium bridging.

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CHAPTER 3

Effect of admixture on the pore structure refinement and enhanced performance of alkali-activated fly ash-slag concrete*

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Time (in days)

Decline of the chloride migration in AAM as an effect of the porosity refinement



Graphical abstract

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Abstract

This paper investigates the influence of a plasticizing admixture on the pore structure refinement of alkali-activated concrete and paste mixtures and the consequently enhanced performance. Alkali-activated fly ash-slag concrete and paste are designed using a polycarboxylate-based admixture with different dosages. The pore structure and porosity are analyzed using mercury intrusion porosimetry (MIP). The workability, compressive strength, chloride migration resistance and electrical resistivity of alkali-activated fly ash-slag concrete and paste are determined. The results show that significantly improved workability and strength development are obtained at an increased admixture content. The admixture improves the gel polymerization product layer most likely around the GGBS particles, densifying the matrix. The 28-day Cl-migration coefficient of admixture (1-2 kg/m³) modified concrete is equal to the reference mixture, while at the highest admixture content the Cl-ingress is increased. At the later ages (91-days), the Cl-migration coefficients of all concretes, non- and admixture-containing samples, are comparable and low (about $2.6 \times 10^{-12} \text{ m}^2/\text{s}$). The MIP analyses show a significant decrease of the total and effective capillary porosity over time at an increased admixture content. The relationships between the porosity and other properties are discussed, at varying admixture contents.

Keywords: alkali activated fly ash-slag concrete, admixture, workability, microstructure, compressive strength, chloride migration, pore structure

1 Introduction

Alkali activated slag/ fly ash based binders in comparison with traditional Portland cement possess comparable to moderately modified material properties (i.e. mechanical strength, chloride ingress, acid and carbonation resistance) [1-4]. Designing alkali activated materials (AAM) with high durability performance largely depends on the mixture composition (design). This is mainly controlled by the applied precursor minerals such as ground granulated blast furnace slag (GGBS) and pulverized coal fly ash (PCFA), and the concentration, type and combination of alkaline activators (i.e. sodium or potassium silicate or hydroxide). More specifically, a higher GGBS content (0 to 100 wt.%) as a replacement of the PCFA in the binder, favors the matrix densification and strength development [5-8]. By forming mainly calcium dominated gel-structures (C-A-S-H), consequently resulting in a reduced chloride migration rate in concrete [9]. However, to support the practical application and further development of AAM as well as that of Portland cement, both materials are strongly dependent on the availability of admixtures [10,11]. Due to the existence of multiple molecular varieties, admixtures (known as superplasticizers (SP's)) can perform very differently in optimizing the fresh concrete mixture state, although this is also dependent on the binder type and composition [12].

For fly ash dominated AAM systems, the mixture workability, setting time and liquid demand can be relatively easily modified by polycarboxylate and naphthalene type admixtures [13–17]. Although often relatively high admixture dosages (\geq 1-10 wt.% in relation to the binder content) are required in order to gain a high mixture flowability and consistency [15,17–19], compared to that of Portland cement mixtures (mostly \leq 1 wt.%). As a consequence, high dosages lead to unwanted negative side effects, such as increased material porosity and loss of mechanical strength [15,17]. For GGBS-dominated AAM, almost all related admixtures often do not sufficiently modify the mixture workability [20]. In some cases, mixture rheology improvement and setting time retardation are observed to a certain extent when using only a hydroxide instead of a silicate based activator [15,20]. Overall, many of these studies indicate that admixtures are able to reduce the liquid to binder ratio or liquid demand of the fresh mixture. Summarizing relevant literature dealing with the effect of mainly Portland cement based admixtures on AAM systems, the following remarks can be drawn:

- Admixtures shows no improvement to the delay of the mixture setting time and overall mixture workability, which could be associated with their physical and chemical incompatibility or rapid chemical oxidation in the high alkali system [13,15,20].
- Admixtures enhance the AAM mixture workability over a short period of time (≤ 10-40 min). An increasing GGBS and silicate activator content strongly reduce the

workability, therefore AAM is often prone to a non-predictable, very rapid decline of the workability and fast setting [15,16,18,20-22].

- Naphthalene and polycarboxylate admixtures are the most effective SPs, to enhance the mixture workability of alkali activated PCFA systems [13,15,16] compared to GGBS based systems [15,18,22,23].
- Admixtures use frequently causes negative effects on the setting time and mechanical property of AAM [13,15–18,20–22,24].
- Admixtures can have either negative or positive effects on the concrete shrinkage [20,24].

Limited experimental studies have been performed on the effect of admixtures on AAM systems as often admixtures are not able to sufficiently modify AAM concrete [20,25]. However, in recent years, more, while still rather limited commercial admixtures, mainly polycarboxylates, are available for AAM. Further knowledge is required in order to improve the physical and chemical understanding of their working mechanisms, as well as that of their predictability with AAM concrete production.

Apart from the rheology modifying ability [14], another positive effect is that the microstructure development of AAM concrete can be significantly enhanced by a polycarboxylate. Through densification of the interfacial transition zone (ITZ) [26], located between the newly formed AAM gel structure and solid particles (binder and the aggregate minerals), at which the porosity is reduced. This leads to the shift of pore size of hardened AAM towards smaller ranges which improves the material performance by for instance a higher material strength, reduced permeability and enhanced ion diffusion resistance (e.g. chloride). However, the microstructure development (i.e. porosity and permeability) and the chloride migration of AAM concrete under the influence of using admixture have not been studied. Research is needed to understand the potential physical and chemical mechanisms affected by a working admixture in concrete, contributing to the design of durable AAM concretes for construction structures.

In the present study, a comprehensive approach is applied to investigate the effect of admixture on the relationship between pore structure refinement and enhanced performance of alkali-activated fly ash-slag concrete. The main objectives of this study are:

- Analyze the influence of the admixture content on the fresh mixture state properties, by measuring the setting time and the workability progression over time;
- Study the influence of the admixture content on the hardened material state properties, by analyzing the AAM compressive strength, chloride migration rate and material electrical resistivity over time;
- Determine the effect of admixture content on the AAM pore structure over time and consequent influence on the material durability (chloride migration);

• Investigate the relation between different system parameters and their significance; such as concrete compressive strength and porosity and their effect on the permeability and chloride migration of concrete over time under the influence of the admixture content.

2 Materials

2.1 Materials

The used mineral binder (MB) is a blend of 73.7 wt.% pulverized coal fly ash (PCFA) class F in accordance with NEN-EN 450 with 25 wt.% granulated ground blast furnace slag (GGBS) and 1.3 wt.% pure sodium meta-silicate pentahydrate powder with a mol. ratio of SiO2 1.50/1.79 Na2O (supplied by PQ, The Netherlands). The chemical composition of the MB is determined by X-ray fluorescence (XRF), as shown in Table 3.1.

Oxides	PCFA	GGBS	MB
SiO ₂	59.7	34.3	51.4
Al ₂ O ₃	24.6	9.8	17.9
CaO	1.5	41.8	13.9
Fe ₂ O ₃	6.8	0.5	6.3
MgO	1.3	7.7	3.8
K ₂ O	3.0	0.6	2.2
Na ₂ O	0.6	<0.1	1.1
TiO ₂	1.2	1.2	1.1
Mn ₃ O ₄	0.0	0.3	0.2
BaO	0.1	0.1	0.1
P_2O_5	0.1	<0.1	0.4
SO ₃	1.0	3.6	1.7
Cl	<0.1	<0.1	<0.1
LOI (950 °C)	0.9		1.6

Table 3.1: Chemical composition (%) of the mineral blended binder (MB), determined with XRF.

LOI: loss of ignition

River aggregates (sand 0-4 mm and gravel 4-16 mm) were used to produce the mixtures. A commercial 33% liquid sodium hydroxide (NaOH) with a molarity (M) of 11.2 was diluted by tap water to obtain the desired (3M NaOH) system alkalinity.

A polycarboxylate plasticizing admixture (supplied by SQAPE Technology), hereafter identified as "admixture", was used to enhance the fresh concrete workability. The polycarboxylate is highly soluble in water and the backbone contains poly-functional reactive side chains, e.g. carboxyl, which initiate the metal (mainly calcium) adsorption reactions. Preliminary research shows that a chemical oxidation effect is observed when mixing this admixture with NaOH solution that helps to improve the workability. The added additional water, NaOH and the admixture were summed as the total liquid volume (although solids are present). The relevant material properties, including the specific density, water absorption and mean particle size (d_{50}), are listed in Table 3.2.

Material	Density (kg/m ³)	Water Absorption (%)	d ₅₀ (μm)
PCFA	2312		20
GGBS	2893		12
Mineral binder (MB)	2498		15
Sand (0-4 mm)	2600	0.80	
Gravel (4-16 mm)	2590	1.80	
Meta silicate powder	900		650 till 900
NaOH solution (33 % pure)	1360		
Admixture	1190		

Table 3.2: Materials characteristics.

* PSD: particle size distribution

2.2 Binder composition and admixture

A predefined AAM binder was used in this study, composing of: (1) the blended mineral binder with meta-silicate and (2) a fixed 3 M NaOH activator. Preliminary research and the literature [27] verified that this relatively low activator molarity is able to effectively promote an acceptable setting time and sufficient mechanical strength performance of AAM concrete. The low silicate powder addition, as a part of the MB, is applied to increases the material strength at the early ages of 1 day to 7 days, while higher silicate dosages (> 1.3 wt.%) would reduce the mixture workability. Additionally, the plasticizing and liquid reducing effects of the admixture on paste mixtures containing sole PCFA or GGBS were examined by performing the water demand experiments [28]. The results showed that a significant decrease of liquid demand up to 25 % for both PCFA and GGBS can be observed. In overall, PCFA shows a lower liquid demand with an overall factor of about 2 of GGBS. Based on the preliminary study, a high PCFA content (\approx 75 wt.%) was used for the mineral binder composition, concerning both the mixture liquid demand and binder performance.

3 Sample preparation

3.1 Concrete mixtures

The concrete mixtures (Table 3.3) were analyzed on workability (slump) and tested on the compressive strength, the chloride migration rate and the material electrical resistivity over time, to evaluate the effect of admixture. The mixtures (140 L per batch) were prepared with a high-speed rotating pan mixer. During the mixture preparation, firstly sand, gravel and the solid precursors were mixed and then the liquid was added. The total mixing time was 5 min: 1 min of dry mixing (sand, gravel with solid precursors) and 4 min of additional mixing (adding the total liquid). Fresh concrete was cast in steel molds (150 × 150 × 150 mm³), finished on a compaction table and sealed with a plastic foil. After 24 hours of room temperature curing, the specimens were demolded, wrapped in with plastic foil and stored at room temperature (≈ 20 °C).

Mixture code	Sand (wt.%)	Gravel (wt.%)	Binder (kg/m ³)	Total liquid (l/m³)	L/B ratio	NaOH (M)	Admixture (kg/m ³)
А	47	53	400	127	0.32	3	0
В	47	53	400	127	0.32	3	1
С	47	53	400	127	0.32	3	2
D	47	53	400	127	0.32	3	3
Е	47	53	400	127	0.32	3	4
F	47	53	400	127	0.32	3	5

Table 3.3: Mixture composition of AAM concretes.

3.2 Paste mixtures

The workability, compressive strength and pore structure of the designed paste mixtures (Table 3.4) were analyzed. Mercury intrusion porosimetry (MIP) was used to evaluate the effect of using admixture on the pore structure development. The paste mixtures have the same L/B ratio (0.32) and 3M NaOH alkalinity as the concrete mixtures; the admixture content per kg binder was identical with that of the tested concrete mixtures A, B, D and F with a corresponding admixture contents of 0/ 1/ 3/ 5 kg/m³. During the sample preparation, all components were mixed at once with a Hobart mixer for 5 min at medium speed. The specimens for strength testing were prepared in polystyrene prism molds ($40 \times 40 \times 160 \text{ mm}^3$), compacted on a vibration table and sealed with plastic foil. For the porosity experiments, fresh paste was cast in plastic containers (\approx 300 ml) and filled to the top and slightly tamped for air release. Sealed containers were placed on a slowly rotating apparatus to avoid particle segregation, and the rotation apparatus was

stopped after paste setting after about 4 hours. The container samples were stored for curing in a climate room (20 °C and \ge 95% RH) until testing.

Mixture	MB (g)	Total liquid (ml)	L/B ratio	NaOH (M)	Admixture (g/kg)	Related concrete mixture design
PO	1000	320	0.32	3	0	А
P1	1000	320	0.32	3	2.5	В
Р3	1000	320	0.32	3	7.5	D
P5	1000	320	0.32	3	12.5	F

Table 3.4: Mixture composition of AAM pastes for porosity experiments.

Admixture content in the paste mixture is multiplied by a factor 2.5, to correspond with the admixture content of the concrete mixtures A, B, D and F (Table 3.3), gaining equal admixture dosage per kg of binder.

3.3 Experimental methods

The slump of the fresh concrete was measured in accordance with NEN-EN 12350-2. During the test period, fresh concrete was mixed at very low rotation speed (imitation of real-life concrete truck transport mixer process). The flowability of the paste mixtures was determined using a Hägermann cone (100 mm base diameter, 70 mm top diameter and height 60 mm), in accordance with EN 459-2.

The compressive strength of concrete was measured at the age of 1, 7, 28 and 56 days respectively in accordance with NEN-EN 12390-3 and the strength of paste samples were performed in accordance with NEN-EN 196-1.

The material electrical resistivity was tested at the age of 28 and 91 days respectively on cubic samples $(150 \times 150 \times 150 \text{ mm}^3)$. The applied method was in accordance with the Two Electrodes Method (TEM) which is described in the reference [29].

The Rapid Chloride Migration (RCM) coefficient of concrete at the age of 28 and 91 days respectively was determined in accordance with the NT Build 492. Samples ($150 \times 150 \times 150 \text{ mm}^3$) were stored until 24 hours after casting in a 20°C water bath, securing maximal water saturation as normally AAM concrete is preferably not cured in a water bath. The experiments were performed on fourfold drilled samples (\emptyset 100 mm).

The porosity measurements were performed with MIP on paste mixtures, measuring the pore sizes from 0.006 to 350 μ m (twofold measurement per sample). The sample preparation procedure was the following: at different ages of 7, 28 and 56 days samples were crushed and the reaction was stopped with liquid nitrogen and then the samples were vacuum freeze dried at -28 °C, until constant mass to allow the pore solution to be removed by sublimation of ice microcrystals and maintaining the microstructure without significant damages. Mercury intrusion started at a low pressure of 0-0.003 MPa followed by a pressure increase from 0.0036 to 210 MPa. The extrusion process started immediately afterwards, during which the pressure decreased from 210 to 0.14

MPa. The surface tension and the contact angle were fixed at 0.485 N/m and 132 degrees, respectively.

4 Results and Discussions

4.1 Effect of admixture on the concrete characteristics

4.1.1 Effect of admixture on the fresh concrete workability

Figure 3.1 shows the fresh concrete slump over time as a function of the admixture content (0 to 5 kg/m³) for concrete mixtures A-F, presented in Table 3.3. The results clearly show a significantly affected slump behavior over time, from a very stiff consistency (concrete consistency class S0) without admixture, to a more fluid and then a highly fluid consistency at higher admixture contents. At a higher admixture content of more than 4 - 5 kg/m³, deformation mechanisms (i.e. segregation and bleeding) of the fresh concrete mixtures were observed. For the tested mixtures, 3 kg/m³ of admixture is identified as the optimum dosage, corresponding with 0.75 wt.% of the binder content.



Figure 3.1: Slump of fresh concrete mixtures A-F between 6 to 120 min versus admixture content.

Further, the admixture was able to control the fresh concrete workability over time, showing a slowly declining slump (6 to 120 min). The slump modification by the admixture is also observed in the previous study [30], applying the polycarboxylate admixture in the production of ultra-lightweight AAM concrete. However, using the admixture with a dosage of ≥ 3 kg/m³, the retention of the slump between 6 to 120 min is clearly observed, implying an extended mixture setting time. This highly effective admixture-related result has been mainly observed in the literature for Portland cement systems [11,12,31]. as admixture use in AAM systems to modify the fresh mixture workability is much less effective [15,18,32]. This can be explained by the increasing

admixture adsorption behavior, as a function of a higher admixture content, onto the positively charged mineral precursor particle surfaces [12,33,34], which is also in detail explained in Chapter 2. This connection keeps the particles sterically at distance enhancing the mixture workability which results in a delay of the microstructure development indicated by a delayed mixture setting (Figure 3.1) and consequently inhibited early age compressive strength progression (Figure 3.2) [35,36].

4.1.2 Effect of admixture on the compressive strength

Figure 3.2 shows the concrete compressive strength development as a function of the admixture content (0 to 5 kg/m³), for mixtures A to F. The results indicate that a higher admixture content retards the early age (1 day) strength development. However at the age of 7 days, all admixture containing concretes exhibit \approx 20 MPa (varying between 18 to 23 MPa), which is higher than the non-admixture reference of 15 MPa. Over time, this effect is even more significant, as the strengths increase more (42-46 MPa at 28 days) in comparison with the reference concrete (20 MPa at 28 days). It should be noted that the lower strength development from the reference concrete (containing no admixture) is attributed to the compaction influence due to its relatively stiff fresh mixture consistency (Figure 3.1). As no significant differences of the visible surface smoothness and measured fresh concrete material density between all tested samples is observed.

A comparable admixture effect on the strength development is also observed in the mortar experiments, described in Chapter 2.



Figure 3.2: Compressive strength development of concretes with varying admixture contents for mixtures A-F. Error bar: deviation of the strength based on 3 concrete samples.

The optimal admixture content with regard to compressive strength is about 3 to 4 kg/m³. The decline in strength with the admixture content of \approx 5 kg/m³ could be explained by the observed mixture segregation, while unstable and inhomogeneous mixtures can

result in a higher concrete porosity and therefore lower strengths. This will be further discussed in Section 4.2.4. However, it is attributed that the use of of admixtures, within an optimal range, improves the mixture workability and particle packing and therefore the concrete densification which consequently leads to an enhanced material strength [37]. However, apart from this, other fundamental physical and chemical admixture-related mechanisms could also be of influence:

- For the early age strength (1 to 7 days): It is known from the literature that a higher (polycarboxylate) admixture content increases and partially controls the precursor element release (mainly calcium) by slowing down the mineral precursor dissolution processes of mainly GGBS [38]. This is initiated by admixture adsorption, due to calcium bridging onto mineral surfaces and element complexation of the admixture (ligand formation) that disrupt nucleation and early age polycondensation. Further, the observed 1 day strength retardation is in line with the prolonged setting time of the fresh concrete, which is increasingly noticeable at higher admixture contents (Figure 3.1).
- For the later age strength (7 to 56 days): It was observed in previous research [39] that the reaction product (gel layer thickness) around GGBS particles within a 28 hardening period, is significantly thicker with admixture compared to a non-admixture reference paste mixture, as shown in Figures 3.3a and 3.3b. This effect has been reported in the literature, on both AAM [14] and Portland cement [26] systems with the enhanced matrix development, by densifying the interfacial transition zone (ITZ) between: (I) the newly formed gel matrix and solid-binder and (II) the newly formed gel matrix and the aggregate particles [26], which can lead towards a modified material strength performance (Figure 3.2). This will be further discussed in Sections 4.2.3 and 4.2.4.



Figure 3.3: ESEM pictures of gel layer thickness around PCFA and GGBS particles within paste samples at 28 days of age of (a) paste without admixture and (b) with admixture (paste mixture comparable with P3). The GGBS particles (red arrow) are overall light grey, rectangular shaped, while PCFA are darker grey, round shaped containing hollow spheres.

4.1.3 Effect of admixture on the Cl-migration

The previous sections demonstrated that the admixture content strongly influences the fresh and hardened state AAM concrete performance over time. Figures 3.4a and 3.4b show the effect of the admixture content (0 to 5 kg/m³) on the Cl-migration coefficient (abbreviation is Drcm) of concrete mixtures A to F, at the age of 28 and 91 days, respectively. At the age of 28 days, the Cl-migration rate in concrete is strongly influenced by the admixture content, as shown in Figure 3.4a. Samples containing 0-2 to about 3 kg/m³ admixture have a comparable and low (approximately $3 \times 10^{-12} \text{ m}^2/\text{s}$) Cl-migration, even though, the initial fresh mixture slump increases significantly as an effect of a higher admixture dosage (Figure 3.1). Additionally, this indicates that the references sample (containing no admixture) possess a high compaction level and related matrix density even though its relative stiff fresh mixture consistency.


Figure 3.4: Chloride migration coefficient of (a) 28 and (b) 91 days old AAM concretes with varying admixture contents for mixtures A-F. The dashed line is the trend line.

Their overall performance (mixtures containing 0-2 to about 3 kg/m³ admixture) is in line with the literature [9], stating that AAM and specifically fly ash-dominated systems can obtain a low Cl-diffusion rate. On the contrary, at a high admixture content of $\geq 3 - 5$ kg/m³, the Cl-migration coefficient strongly increases at which these three D_{rem} values are followed by a perfect exponential trend (R: 1.00). This increase, is probably related to a higher porosity or abundance of capillary pores caused by the segregation, consequently higher permeability of the concrete that strongly influences the Cl-migration [9]. This effect can also be compared with a higher liquid content or higher L/B ratio, which also significantly increases the porosity [40]. The AAM porosity properties is further discussed in Section 4.2.3, in addition further study is needed to gain more understanding of the observed results. For the 91 days results (Figure 3.4b), all concrete mixtures (non- to high admixture contents) show a decrease in Clmigration, towards a comparable and low level of about 2.6×10^{-12} m²/s. Surprisingly, mixtures with an admixture content $\geq 3 \text{ kg/m}^3$ show the most significant Cl migration coefficient decline. This effect can be assumed to be controlled by the element dissolution behavior of PCFA in the binder, favoring a further densification of the matrix [9,41] and consequently improved strength (Figure 3.2), resulting in a reduced diffusion rate. This effect is also observed in the literature [42–45], showing that the matrix of AAM and Portland cement based mixture, containing PCFA, significantly densifies in the period of 28 to 91 days after casting. Additionally, material electrical resistivity served in this study as a quick and reliable indicator to determine the concrete permeability and related Cl-migration performance [29]. Figure 3.5 shows the Cl-migration coefficient in relation with the material electrical resistivity of 28 and 91 days old AAM concrete mixtures A to F.



Figure 3.5: The relation between Cl-migration rate (Drcm) and material resistivity of AAM concretes at 28 and 91 days for mixtures A-F. The numbers close to data points are the admixture content (g/ kg). All samples' pH range between 12.0 to 12.5.

The results show a significant resistivity increase when increasing the concrete age from 28 to 91 days, as well as a decreased Drcm over time. This behavior is comparable with Portland slag cement mixtures [29], although overall the AAM concrete mixtures exhibit far lower resistivity values. in comparison, at 28 days the Portland cement mixtures show RCM values ranging between about $1 - 5 \times 10^{-12}$ m²/s with an electrical resistivity ranging between 175 - 500 Ω m [29], where the representative AAM value range between about $2 -5 \times 10^{-12}$ m²/s with a resistivity ranging between 60 - 175 Ω m. This difference in resistivity between both systems is maintained when the age of the concrete increases. Further, the electrical resistivity of both systems strongly increase, which is an indication of further material densification and consequently lower permeability. The Cl-migration and electrical resistivity results also indicate that the effect of the admixture content is related to the porosity development of paste and accordingly of concrete samples (further discussed in Section 5).

4.2 Effect of admixture on the paste characteristics

4.2.1 Effect of admixture on the fresh paste flowability

The paste slump was measured directly after mixing and showed a similar behavior (flowability modifying effect) as observed in the concrete mixtures (Figure 3.1). An

increase of paste flowability as a function of admixture content: 0/1/3/5 g/kg admixture resulted in a slump of 200/230/240/250 mm, respectively (obtained data points follow a logarithmic trend (R: 0.95)).



Figure 3.6: Compressive strength development of AAM paste mixtures P0-P5 versus admixture content.

4.2.2 Effect of admixture on the compressive strength

Figure 3.6 plots the compressive strength development of paste as a function of the admixture content (0 to 5 g/kg binder) for mixtures P0 to P5, which are described in Table 3.4. A higher admixture content slightly retards the early age strength development. While at 28 days, the strength is increased when increasing the admixture content. The admixture related strength development shows strong similarities with that of the tested concrete mixtures, as described in Section 4.1.2. Additionally, the paste slump, measured directly after mixing, shows a similar behavior (flowability modifying effect) observed for the concrete mixtures due to the increase of the flowability at an increased admixture dosage. It should be noted that difference in strength increase in paste and concrete is obverted, which might be attributed to several reasons, including aggregate type and content, workability, compaction effort and particle packing.

4.2.3 Effect of admixture on the porosity

Figures 3.7 till 3.9 show the development of the AAM paste porosity (7 to 56 days) of medium to large pore size (0.01 to 100 μ m), as a function of the admixture content (0 to 5 g/kg binder) for mixtures P0 to P5. It is shown in Figure 3.7 that after 7 days AAM pastes with 0 and 1 g/kg admixture have a similar size pore distribution. However, at high admixture contents (3 to 5 g/kg), larger pores are observed in the paste mixtures, which is shown (Figure 3.7b) by an extreme growth (hump) for 1-2 μ m pores. At the age of 28 to 56 days (Figures 3.8 and 3.9), this hump completely disappears for all samples,

only pores with smaller size or a refined porosity are observed. The results also show a more refined paste pore structure as a function of the increasing admixture content.



Figure 3.7: Pore size distribution at 7 days of age of AAM paste for mixtures P0-P5, with a varying admixture content: (a) pore size distribution; (b) pore size distribution differential curve.



Figure 3.8: Pore size distribution at 28 days of age of AAM paste mixtures P0-P5 with varying admixture content: (a) pore size distribution; (b) pore size distribution differential curve.



Figure 3.9: Pore size distribution at 56 days of age of AAM paste mixtures P0-P5 with varying admixture contents: (a) pore size distribution; (b) pore size distribution differential curve.

Two distinct pore types are identified as being critical with regard to material strength and liquid and ion transport for paste or concrete: (1) effective capillary pores that vary between 0.01 to 10 μ m (10 to 10.000 nm) and (2) gel pores with a size < 0.01 μ m (< 10 nm) [46,47]. Figures 3.10a and 3.10b show the total and effective capillary porosity

development (7 to 56 days) of AAM pastes, as a function of the admixture content (0 to 5 g/kg binder) for mixtures P0 to P5.



Figure 3.10: Porosity development at 7/ 28/ 56 days of age of AAM paste mixtures P0-P5 with varying admixture contents: (a) Effective capillary porosity; (b) Total porosity.

With regard to the total porosity (Figure 3.10a), all samples show similar values after 7 days of curing. However, over time after 28 and 56 days, the total porosity is significantly decreased at an increasing admixture content, following a logarithmic trend. The measured porosity of the non-admixture containing reference mixture (P0) is in line with the literature [7]. A different behavior is observed for the effective capillary porosity (Figure 3.10b). At 7 days, an increase in effective capillary porosity is related to a higher admixture content (followed by a linear trend). However, further over time at 28 to 56 days, this effect is altered, where a lower effective capillary porosity is obtained at an increasing admixture content (followed by a logarithmic trend). This admixture effect of pore structure refinement in AAM has never been reported in the literature. Often a reduced porosity over time in AAM is observed, when a higher GGBS binder content instead of PCFA and or alkaline activator (silicate source) is used [41]. In addition, Figure 3.11 shows the relation between the total porosity and the effective capillary porosity dependent on the admixture content over time for AAM pastes (original data of Figs 10a,b). The results show a strong decrease of the total porosity at a decreasing effective capillary porosity over time with a higher admixture content, following a logarithmic trend.



Figure 3.11: Correlation between total and effective capillary porosity at 7, 28 and 56 days of age for AAM paste for mixtures P0-P5. Values close to the data points are the admixture content (g/kg).

4.2.4 Porosity versus strength progression

Figure 3.12 shows the relation and prediction (trend) between the total and effective capillary paste porosity and the paste compressive strengths over time. Firstly, a higher admixture content results in a lower total and effective capillary porosity over time at the age of 28 days and therefore increases the material strength. Secondly, the relation between strength and porosity of cement-based (porous) materials such as AAM can be predicted by using a (non)-linear trend. As a linear trend sometimes overestimates the results and the literature [48] indicates that both porosity parameters follow a different trend to explain the strength. For the total porosity, a linear trend is used and for the effective capillary porosity a logarithmic trend is derived. Both findings are in line with the literature on Portland cement mortars [48].



Figure 3.12: Correlations between: paste compressive strength and the total and effective capillary paste porosities over time (7 to 28 days age) for mixtures P0-P5. Values close the 28 days data points are the admixture contents (g/kg). Fitted lines are based on data point at 28 days of age.

5 Discussions

The results presented in the previous sections on paste and concrete mixtures show that the use of a plasticizing admixture enhances the flowability properties and the hardened state performance of AAM. Figure 3.13 shows the relation between the Cl-migration coefficient (Drcm) at 28 days of AAM concretes and the total and effective capillary porosity of AAM pastes at 28 days. From this correlation it can be concluded that AAM concretes with a low to optimal admixture content (1 to 3 kg/m³) possesses a low Cl-migration rate and related material electrical resistivity as shown in Figure 3.5, indicating a low permeability. This is in line with the significant pore structure refinement over time as shown in Figures 3.7 to 3.9. This refinement is significantly enhanced by admixture with a proper dosage, as the ingress of Cl-ions is largely controlled by the concrete permeability which is influenced by the porosity while excessive admixture amount leads to segregation and higher porosity [41,43,44]. Furthermore, this AAM matrix densification effect by using admixture is supported by the literature on Portland cement mixtures [37], and this effect is observed and detailed analyzed in the previous study [39] of AAM paste mixtures, as shown in Figure 3.3. Where scanning electron microscopy (SEM) analysis showed that the matrix of a AAM paste, at 28 days age (containing about 3 kg/m³ of admixture, which is found to be the optimal content in the present study), has a significantly thicker ($\approx 34\%$) newly formed gel layer around the GGBS particles instead of the non-admixture reference samples. This leads to a more densified and lower permeable AAM matrix with a significantly higher compressive strength (supported by Figure 3.2), which is strongly related to a lower total porosity as supported by Figure 3.12.



Figure 3.13: Chloride migration of 28 days old AAM concretes (mixtures A/B/D/F of Table 3.3) in relation to the total and effective capillary porosity of 28 days old AAM pastes (mixtures P0-P5). Values close to the data points are the admixture contents (g/kg in paste and kg/m³ in concrete).

The plotted data in Figure 3.13 show that both the total and effective paste porosity within a defined range have comparable influences on the Cl-migration in concrete. No distinct trend can be observed between both porosity parameters and their individual influences on Cl-migration, which can be explained by the fact that both parameters at 28 days age are strongly related with each other (Figure 3.11). However, data obtained from a preliminary study [49] on a 28-day old admixture-modified AAM concrete (mixture comparable with AAM mixture D using 3 kg/m³ of admixture), show a relatively high abundance of connected spherical voids in the matrix. This is supported by the literature [43,47], reporting that the matrix permeability of PCFA-dominated AAM and Portland cement pastes is strongly related with the effective capillary porosity. Since the connected pores provide a continuous channel for transport, they largely affect the permeability and the ion ingress in the matrix [43,44]. It should be noted that the porosities shown in Figure 3.13 were acquired from paste sample while the Cl-migration results were based on concrete samples. As mentioned in Section 4.1.1, a higher admixture dosage than 3 kg/m³ results in concrete segregation that leads to a clearly increased Cl-migration (mixture 5 in Figure 3.13). Nevertheless, it can be concluded that both total porosity and effective capillary porosity can be used to indicate the Cl-migration property in AAM.

6 Conclusions

The effects of a polycarboxylate admixture on the flowability properties and hardened state performance of AAM concrete and paste mixtures are investigated. The relations between the alteration of the pore structure and related material strength and chloride ingress that are changed, dependent on the admixture content, are evaluated. Based on the obtained results, the following conclusions can be drawn:

- The workability of the fresh AAM concrete significantly improves from a zero slump towards a maximal measurable slump value (> 250 mm) with a relatively low admixture content (0.25-0.75 wt.% of the binder). At which it is likely that the setting time of the concrete mixture is increasingly prolonged with a higher admixture content, even up to 120 min at an admixture content of about 3 kg/m³.
- The concrete compressive strength progresses significantly over time at higher admixture contents. The 7 and 28 days compressive strength of admixture-containing concrete (at an optimal admixture content (3 to 4 kg/m³)) are about 22 and 44 MPa, respectively, while that of the reference concrete are only 15 and 23 MPa, respectively.
- The pore structure of the AAM paste mixtures is strongly refined over time at an increasing admixture content, resulting in a significant decrease of the total and effective capillary porosity and reduced material permeability. A significant relation is found between the compressive strength and the porosity.
- The chloride migration coefficients of admixture-modified AAM concrete at the age of 28 and 91 days, at an optimal admixture content, are about 3.0×10^{-12} m²/s and 2.6×10^{-12} m²/s, respectively. A relationship between the Cl-migration coefficient (Drcm) and material electrical resistivity (Ω m) over time is derived for the AAM concrete mixtures.

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CHAPTER 4

Design and performance evaluation of ultra-lightweight alkali activated concrete*

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Graphical abstract

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Abstract

This chapter presents the development of a sustainable ultra-lightweight alkali activated concrete (with a dry density $\leq 800 \text{ kg/m}^3$) for both thermal insulating and load bearing purposes. A predesigned mineral precursor resulted from industrial by-products is used as the raw material for alkali activation and NaOH with a low concentration of 2-3 M is used as the alkali activator, together with a specially designed admixture as superplasticizer. The ultra-lightweight property is achieved by applying a waste glass produced expanded lightweight material as aggregates. The effects of influential parameters including the design approach, liquid/binder ratio, binder/aggregate ratio, particle size and air entraining agent on the properties of the designed concrete are evaluated. An ultra-lightweight concrete with a proper workability is obtained and the hardened concrete shows excellence performances in terms of mechanical property, thermal property and durability. At a moderate compressive strength (10 MPa), an excellent thermal conductivity of 0.11 W/(m·K) is resulted. Furthermore, a very low thermal conductivity of 0.07 W/(m·K) is reached at a compressive strength of 8 MPa, indicating great potential for the production of a load bearing and highly insulating building material as an alternative for the traditional materials.

Keywords: ultra-lightweight concrete, industrial by-products, alkali activated materials, compressive strength, thermal conductivity, water permeability.

1 Introduction

In general two types of alkali activated materials (AAM) can be classified: (I) the high calcium system, with ground granulated blast furnace slag (GGBS) as a typical precursor, having a C-A-S-H type gel as the main reaction product [1]; (II) the low calcium system with Class F pulverized coal fly ash (PCFA) and metakaolin as representative raw materials, having N-A-S-H type gels within a three-dimensional network as the major reaction product [2]. Extensive research has been performed on these two systems as binder system for building material (concrete) production, including for instance the role of activator type and alkali concentration [3], the effect of the dosage of raw materials [4], the effect of admixtures [5,6], the curing effect [7], microstructure, mechanical properties, thermal properties and durability [8]. However, although excellent performances can be achieved from both AAM systems, drawbacks such as fast setting, relative high shrinkage of specially alkali activated slag [9], and relatively long setting times of specially alkali activated aluminosilicates, could limit the practical application. Research on overcoming these disadvantages is being widely explored and one promising solution is the blended alkaline systems (Na₂O-CaO-Al₂O₃-SiO₂ systems) that are produced by mixing calcium enriched precursors (GGBS) and aluminosilicates (PCFA or metakaoline) [10–15].

Lightweight aggregates concrete (LWAC) has its roots in the ancient period about 3000 years ago when volcanic materials were used as lightweight aggregates [16]. Because of its many advantages such as low density, good thermal insulation, good fire resistance and reduced cost of transport, LWAC has been widely investigated and developed in a wide range of unit weights and suitable strengths for various applications as both structural and non-structural material [17]. In the previous research, a mixture design methodology based on the optimized packing principle was proposed for designing both structural concrete (dry material density \approx 1500 kg/m³) [17] and non-structural concrete (dry material density \approx 650 kg/m³, also called ultra-lightweight concrete) [18], using Portland cement as the binder. The obtained excellent results indicates the validity of the applied design approach as well as the superior performance of the developed Portland cement based concretes.

In addition applying an alkali activated binders to develop lightweight concrete has been investigated. Recycled lightweight block was used as aggregates and alkali activators such as Ca(OH)₂, Mg(NO₃)₂, Ca(OH)₂ and Na₂SiO₃ and PCFA and GGBS as raw material in producing lightweight AAM concrete [19,20]. Results show at a density of \approx 1500 kg/m³, a 28 day compressive of \approx 13 MPa is obtained, while at a density of \approx 1000 kg/m³, a very low value of \approx 2 MPa is resulted [19]. As well as another study studies showed a 28 day compressive strength of \approx 0.5-2.0 MPa and thermal conductivity (TC) of \approx 0.09-0.13 W/(m·K) with a density range of 325-500 kg/m³ [20]. Liu et al. [21] reported an average pore size of 1 mm and the compressive strength between

7-10 MPa when the porosity decreases from 85 % to 40 % in a phosphoric acid based porous geopolymers using aluminium powder as a foaming agent. Lightweight concrete using activated metakaolin-PCFA as binder and aluminium powder to achieve the low densities was designed [22]. The compressive strength is strongly affected by the density, namely between 11.0 and 14.6 MPa at the density of 1200 kg/m² while 3.0-6.4 MPa at 900 kg/m³ and only 1.3-1.8 MPa at 600 kg/m³. Higher curing temperatures of up to 75 °C, are observed to accelerate the early age strength development during the first day but in the long term no difference is observed. Thermal conductivity on the other hand, is positively influenced by the reduced density, yielding 1.22, 0.62 and 0.49 W/ (m·K) at the density of 1200, 900 and 600 kg/m³, respectively. Vaou et al. [23] designed a thermal insulating geopolymer using NaOH as activator, perlite as raw material and hydrogen peroxide as a foaming agent. The thermal conductivity reduces from 0.05 to 0.03 W/(m-K) when the hydrogen peroxide dosage increases from 0.6% to 2.0% by mass of the paste, and remains constant at a further increase of hydrogen peroxide until 2.9%, while in the meantime, the compressive strength increases from 0.3 to 0.8 MPa and then remains stable. Sanjayan et al. [24] reported a lightweight aerated geopolymer concrete with a compressive strength of 0.9 to 4.35 MPa at the density range of 403-1309 kg/m³. They found that aerating of geopolymers causes damages in stoichiometry of alkali activator and incomplete geopolymerization of PCFA particles. Zuda et al. [25] developed alkali activated lightweight composite using water glass as activator, slag as raw material and vermiculite as lightweight aggregates. The composites, with a compressive strength of 22.6 MPa at a dry density of 1918 kg/m³, enable a fast removal of water vapor and other gaseous compounds leading to improved fire resistance properties because of their relatively high water diffusion coefficient. Alengaram et al. [26] observed an increased PCFA content causes the strength reduction due to its higher water demand and a pre-soaking of the used lightweight aggregates is observed to slightly contribute to the strength development in geopolymer lightweight concrete using oil palm shell as lightweight aggregates, PCFA as the raw material and NaOH modified Na_2SiO_3 as activator.

This thorough review indicates the potential of designing lightweight geopolymer concrete. Nevertheless, it can be seen that many available research focused on using foaming agent for the lightweight purpose, which has certain drawbacks. In overall the resulted concrete is very weak in terms of strength, for instance at a density of 900 kg/m³, most of the concretes show a 28 day compressive strength of lower than 5 MPa, and the pore sizes of these concretes are very big, indicating a very high permeability. In addition, the very fast setting of the aerated concrete results in an un-efficient use of the raw materials. In our previous research, an unique ultra-lightweight PC concrete (ULW-PC) applying lightweight expanded glass aggregates (LWA) was developed [18]. The ULW-PC material shows an average fresh material density of ≈ 800 kg/m³, 28 day compressive strengths of ≈ 10 MPa and a thermal conductivity of ≈ 0.12 W/(m·K) [18].

This is, to the authors' knowledge, the concrete with the lowest TC at this compressive strength and density class [27-29]. This type of concrete can be used to design more energy and ecology efficient buildings. For example, the traditional building concepts e.g., multilayer wall approach for utility construction (composed of an outside-, insulation- and indoor layer) could be replaced by a monolithic ULW-PC, resulting in more design flexibility for architects and reduced construction time. Therefore, motivated by this concept and starting from the reported literature, this study aims to develop an ultra-lightweight alkali activated concrete (ULW-AAM) that would bring further the sustainable and innovative development. In this chapter, an ultra-lightweight alkali activated concrete is designed and analyzed, implementing alkali activated binders. A predesigned alkali activated precursor consisting of the mixture of low calcium PCFA and ground granulated blast furnace slag together with sodium hydroxide solution in combination with a plasticizing admixture is applied as the binder. Furthermore, expanded ultra-lightweight material, produced out of waste glass is applied as aggregate. The mixture designs are modified on the basis of multiple steering parameters, whereas the previous research is taken a reference [18]. The following topics are addressed in this chapter:

- The mixture design approach in terms of fresh concrete stability, workability, compressive strength and thermal conductivity of hardened concrete.
- Pre-soaking of LWA, addressing the potential particle segregation in fresh concrete;
- Fresh ULW-AAM concrete workability and strength development characteristics, in relation to liquid binder content (L/B).
- Analyses of optimal binder contents, for optimization of compressive strength and related TC.
- Influence of LWA particle size fractions on ULW-AAM compressive strength and TC.
- The optimal alkali dosage in the activator in terms of compressive strength.
- The effect of air entraining agent, for further reducing density and related TC.
- Element release (Si, Al, Ca, K) from raw materials (minerals) in an alkaline environment, which function as the main AAM gel network building blocks.

2 Materials

The ULW-AAM was designed using a predefined alkali activated binder, supplied by SQAPE Technology, located in The Netherlands. This binder system (mineral precursor, alkali concentration and admixture) possesses comparable mechanical properties with cement (e.g. CEM III/B 42.5 N) according to the preliminary research. The precursor used in this study was pre-mixed in a mineral blended binder (MB), the composition was 73.7 wt.% pulverized coal fly ash (PCFA) class F in accordance with NEN-EN 450 with 25 wt.% granulated ground blast furnace slag (GGBS) and 1.3 wt.% technical

grade sodium meta-silicate pentahydrate powder (supplied by PQ, The Netherlands). This MB has a specific density of 2498 kg/m³, a median particle size (d_{50}) of 15 µm (comparable to for instance CEM I) and a chemical composition of the precursors and the MB are listed in Table 4.1.

Oxides	PCFA	GGBS	MB
SiO ₂	59.7	34.3	51.4
Al ₂ O ₃	24.6	9.8	17.9
CaO	1.5	41.8	13.9
Fe ₂ O ₃	6.8	0.5	6.3
MgO	1.3	7.7	3.8
K ₂ O	3.0	0.6	2.2
Na ₂ O	0.6	<0.1	1.1
TiO ₂	1.2	1.2	1.1
Mn ₃ O ₄	0.0	0.3	0.2
BaO	0.1	0.1	0.1
P_2O_5	0.1	<0.1	0.4
SO ₃	1.0	3.6	1.7
Cl	<0.1	<0.1	<0.1
LOI (950 °C)	0.9		1.6

Table 4.1: Elemental composition (%) of the mineral binder (MB), determined with XRF.

LOI: loss of ignition

The alkali activating solution was formulated by blending water with sodium hydroxide (NaOH), which has a density of 1.36 kg/l and a molarity (M) of 11.2, to a desired molarity (2 or 3M). Furthermore, a plasticizing polycarboxylate admixture (hereafter identified as Ad.) was used with a fixed dosage of 3 l/m³ (supplied by SQAPE Technology). This polycarboxylate admixture improves the fresh concrete workability and related hardened material properties. Furthermore, an air entraining agent (AEA) (supplied by SQAPE Technology) was applied (3 l/m³). The AEA introduces more micro air bubbles into the concrete which could result in a reduced density and a lower TC. In overall, water, NaOH and admixture were addressed as the total liquid in this study (although it contains solids). Additionally, the concrete further consists of various fractions of highly porous expanded glass lightweight aggregates (LWA), supplier Liaver. These are produced out of recycled glass (material properties given by producer, listed in Table 4.2) and possess ultra-low densities (between 300-540 kg/m³) compared to

normal density sand and gravel aggregates (2600 kg/m³). These LWA contain a number of air pores (cellular structure) encapsulated in rather closed and impermeable outer shells. In addition, the differences between the size fractions resulted in different pore sizes i.e. bigger particles contain bigger pores compared to smaller particles.

LWA fraction (mm)	Particle density* (kg/m ³)	Crushing resistance* (MPa)	Thermal conductivity* (W/(m·K))	Water absorption after 30 min (wt.%)	Water absorption after 24 h (wt.%)
0.25-0.5	540	2.9	n.a.	n.a.	n.a.
0.5-1.0	450	2.6	n.a.	5	15.1
1.0-2.0	350	2.4	n.a.	5.7	15.1
2.0-4.0	310	2.2	0.07	4.7	14.4
4.0-8.0	300	1.9	0.07	n.a.	n.a.

Table 4.2: General material properties of LWA.

n.a.: not available/ * provided by the supplier.

Furthermore, the pores of the LWA are mostly closed (not interlinked) and the LWA possess a rather closed outer surface and cellular internal structure, as illustrated in Figure 4.1.



Figure 4.1: SEM picture of LWA: (a) outer surface and (b) cellular pore structure [23].

The particles contribute to concrete with a low density, low TC and relatively high compressive strength, as demonstrated in the research on ULW-PC [18]. Furthermore, their glassy structure and origin, which could be amorphous, might contribute to the gel network condensation process by introducing a pozzolanic reaction [30,31].

3 Design methodology

The ULW-AAM mixture design and composition calculations were performed with a specially developed model, partly based on the modified Andreasen and Andersen model which is applied in the previous research [18,32-35]. As discussed in Section 1, the influence of multiple variables on the properties of the ULW-AAM is studied. The purpose is to design a concrete with a workable fresh behavior and a 28 day compressive strength \geq 10 MPa and low TC \leq 0.12 W/(m·K). In addition, two different mixture design approaches were analyzed, firstly were designed based on sub-optimized packing principle and secondly on optimized packing following the modified Andreasen and Andersen model [18]. By simply adjusting the proportion between smaller and bigger particles, in favor of the bigger particles, a mixture with an sub-optimized packing is resulted which leads to a higher porosity and related lower TC, but also possibly lower mechanical property. An optimized packing of the involved solids (applying fine up to coarse materials to obtain an overall optimal particle packing) results in the lowest porosity, which contributes to an enhanced mechanical property. Both approaches were applied to gain more insight of the fresh and hardened materials properties, and various mixtures were designed and tested, as listed in Table 4.3. In mixtures AAM-A1-5 90-95 % 2-4 mm LWA and 5-10 % 0.25-0.5 and 0.5-1.0 mm LWA are applied (as denoted with * in Table 4.3). AAM-C1 is equal to AAM-B2 and AAM-D1 is equal to AAM-C2, being listed twice only for clarification purposes.

Mix	Binder	Liquid	NaOH	Ad	AEA	LWA (size in mm; amount in kg)				
	(kg)	(1)	(M)	(1)	(1)	4-8	2-4	1-2	0.5-1	0.25-0.5
AAM-A1-5*	450	160	3	3	-	-	*	-	*	*
AAM-A6	450	180	3	3	-	-	188	-	-	17
AAM-A7 (pre-soaked LWA)	450	160	3	3	-	-	184	-	30	-
AAM-B1	492	140	3	3	-	70	57	33	43	29
AAM-B2	492	150	3	3	-	69	57	33	43	29
AAM-B3	492	160	3	3	-	68	56	32	42	28
AAM-B4	492	175	3	3	-	66	54	32	41	27
AAM-C1	492	150	3	3	-	69	57	33	43	29
AAM-C2	492	150	3	3	-	-	127	33	43	29
AAM-C3	400	140	3	3	-	74	61	36	46	31
AAM-C4	400	140	3	3	-	-	136	36	46	31
AAM-D1	492	150	3	3	-	-	127	33	43	29
AAM-D2	457	139	3	3	3	-	118	31	40	27
AAM-E1	388	174	3	3	-	-	54	68	34	122
AAM-E2	388	174	2	3	-	-	54	68	34	122

Table 4.3: ULW-AAM mixture designs (per m³).

Below a brief explanation of the various mixtures is given:

- Mixtures AAM-A1-6: the properties of designs following sub-optimized packing principle are evaluated.
- Mixture AAM-A7: the effect of pre-soaking the LWA is analyzed.
- Mixture AAM-B-E: the properties of mixtures designed applying the optimized-packing approach are determined.
- Mixtures AAM-B1-B4: the effect of liquid-binder (L/B) ratios is studied.
- Mixtures AAM-C1-C4: the effects of binder-aggregate (B/A) ratios and LWA sizes are studied.
- Mixtures AAM-D1-2: the effect of an AEA in concrete is studied.
- Mixtures AAM-E1-2: the effect of NaOH molarity (M) on strength development is studied.
- Additionally, pozzolanic potential and element release of PCFA, GGBS, LWA, glass and sand within alkaline conditions are studied.

The AAM mixtures were prepared as follows: the water, NaOH, AEA (if any) and the admixture were blended. When pre-soaked LWA were applied, particles were placed in water for one hour. Afterwards, the particles were separated from the remaining water by a sieve and surface-dried with paper towels. The mineral precursor and LWA were mixed in a concrete mixer, and the liquid was added. The total mixing time was 7 min. The rotation speed of the mixer was lowered to a comparable speed of truck mixers when the workability was measured over time. After mixing, the fresh concrete was poured into $100 \times 100 \times 100 \text{ mm}^3$ and $150 \times 150 \times 150 \text{ mm}^3$ steel moulds and compacted for 20 seconds using a vibration table. The samples were covered with plastic foil and stored at an ambient temperature of $\pm 20 \text{ °C}$ for 24 h, before demoulded. Subsequently, samples were wrapped in foil and further cured at ambient temperature of $\pm 20 \text{ °C}$.

4 Experimental methods

The workability of the fresh concrete was measured in terms of flow (F) and slump (S), in accordance with NEN-EN 12350-8:2009 [36] and EN 12350-2: 2009 [37]. The initial flow without jolting was also measured, in response to the interest of practice even though this measurement is primarily intended for self-compacting concrete. The fresh concrete density was measured with a 3 litter steel cylindrical mould. The compressive strength tests were conducted to three $100 \times 100 \times 100 \text{ mm}^3$ samples of each recipe at 7 and 28 days with a controlled testing machine (Ratio-Tec). The oven-dry density was determined by drying the samples ($100 \times 100 \times 100 \text{ mm}^3$) at 105 ± 5 °C, following EN 12390-7:2009 [38]. The thermal conductivity (TC) was determined twice on two oven-dried samples ($100 \times 100 \text{ mm}^3$) by a heat transfer analyzer (ISOMET

model 2104). The analyzer applies a dynamic measurement method to determine simultaneously the volumetric heat capacity $(J/(m^3 \cdot K))$ and the thermal conductivity $(W/(m \cdot K))$ of materials with a measurement time of \approx 8-16 min. The measurement is based on the analysis of the temperature response of the tested sample to heat flow impulses, while the heat flow is excited by electrical heating of a resistor heater inserted into the probe which is in direct contact with the test sample.

The water penetration under pressure was measured on three samples of $150 \times 150 \times 150 \text{ mm}^3$ after 28 days of curing. The samples were exposed to 5 bars water pressure for 72 h and the samples were split afterwards, in accordance with EN 12390-8:2009 [36]. The total element leaching experiment was carried out on dry materials, two powders; PCFA and GGBS and three aggregates; natural sand 0-4 mm, recycled glass fraction 0-4 mm and crushed LWA 0-4 mm. All materials were mixed in a 3 M NaOH solution (mixture of demineralized (demi) water and concentrated NaOH) in total volume of 200 ml with an L/S of 5. The samples were shaken for 24 h and the eluate was filtered on 0.45 µm paper. In total 40 ml eluate was acidified with 9ml nitric acid (70 %), to a pH below 2. The method was mainly based on NEN-EN 12457-3 [39] (compliance test for granular samples). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used for the total element analysis of the acidified eluate samples.

5 Results and discussions

The influences of individual parameters on the performance of ULW-AAM are addressed in this section. From the tested two design approaches (one based on optimized particle packing and another one not), the overall performance of the sub-optimized packing approach is not convincing and mixtures were found instable. The results are described in Section 4.1. The results of the mixtures designed based on the optimized packing principle possess stable and predictable performances. This mixture design approach is further applied to analyze the effects of the various parameters (L/B ratio and binder/ LWA ratio influences, LWA fraction size performance, AEA use, activator alkalinity) on the performance of ULW-AAM.

5.1 Mixtures based on an sub-optimized particle packing approach

In preliminary tests the maximum dosage of large LWA particles (fraction 2-4 mm) was determined. Based on this measurement, mixture design is further constructed by filling the remaining voids with fractions of LWA 0-1 mm under a fixed binder dosage. To assess the effect of such an sub-optimized packing approach, the aggregates consist of 90-95 % large (i.e. 2-4 mm) and 5-10 % small (i.e. 0-1 mm) size aggregate fractions. When the concrete was produced (mixture AAM-A1-A5, Table 4.3), the overall workability was poor and almost zero slump was encountered. Furthermore, the system tends to be very sensitive to particle segregation when increasing the liquid from 160 to 180 l/m³.

The additional fresh concrete compaction was insufficient due to firstly, at a low liquid content (e.g. 160 l/m³) the concrete was too stiff to generate an optimal compaction level and secondly, with a higher content (180 l/m³) it shows particle segregation making the mixture unstable. The final concrete contains many large air bubbles, both in the concrete matrix and on the surface. A picture of the cross section of an ULW-AAM by an sub-optimized packing approach is shown in Figure 4.2a.





Figure 4.2: Cross section of ULW-AAM: design using: sub-optimized (a) and optimized (b) particle packing approach.

The samples have the following performances: fresh density of around 830 kg/m³, ovendry density of around 710 kg/m³, 28 day compressive strength of 8-10 MPa, thermal conductivity of 0.153-0.232 W/(m·K) and water penetration of 16-26 mm. The thermal conductivity is low at this strength and density class compared with ordinary building materials due to the cellular internal structure of the LWA (see the SEM pictures in Figure 4.1). However, in overall, the performance of the mixtures designed based on an sub-optimize packing applying dry LWA are found to be insufficient (i.e. poor compaction and a higher thermal conductivity compared to the ULW-PC based on cement) and therefore this design approach is not further tested.

5.1.1 Effect of pre-soaking LWA

The water absorption experiments show that the aggregate absorbs more liquid over time compared to natural sand of gravel (Table 4.2), even though the SEM pictures in Figure 4.1 show a rather closed outer surface. As stated, when dry LWA are applied in sub-optimized packing mixtures, large air bubbles occur or segregation takes place. Applying water pre-soaked LWA may avoid segregation and may contribute to more stable mixture and better compactible concrete. By pre-soaking, less paste will be absorbed from the fresh concrete which strongly affects the workability in time as LWA are already partly saturated. As a consequence, the workability may improve since more liquid is then available to provide workability. However, it has to be taken into account that an effective pre-soaking of LWA is difficult to achieve due to the very small particle sizes and low density (± 300-500 kg/m³). Additionally, from trials it is observed that the dry LWA may absorb a large amount of liquid. As a rule of thumb it can be assessed, that increasing the LWA particle size means a higher absorption. In mixture AAM-A7 (Table 4.3) it is observed that the pre-soaked LWA in the mixture generated more reliable characteristics compared to the non-presoaking mixtures in terms of stability, compaction, air content, porosity and particle distribution. Still its overall fresh and hardened state performances are poorer than expected. The concrete has the properties: fresh density of 850 kg/m³, oven-dry density of 687 kg/m³, 28 day compressive strength of 9.1 MPa and TC of 0.133 W/(m·K).

5.2 Mixtures based on an optimized particle packing approach

The mixture design methodology based on an optimized particle packing approach has been addressed in detail in the previous research [18,32–35]. The mixture designed based on the optimized packing approach (AAM-B-E, Table 4.3) show overall better and stable fresh and hardened concrete properties in terms of stability, compaction and porosity. A picture of the cross section of a hardened mixture is illustrated in Figure 4.2b. It is shown that less air bubbles are present in the mixture, the particles are distributed more homogeneously in the matrix and the small LWA fill up the area between the bigger particles which results in a more stable specimen.

5.2.1 Effect of liquid/binder ratio

Within common concrete practice, the modification of fresh concrete workability is mainly influenced and controlled by three parameters, including total solid particle packing, liquid content and admixtures. In this study the influence of liquid content on the fresh ULW-AAM workability is mainly addressed by varying the L/B ratio from 0.28 to 0.36 (AAM-B1-4, Table 4.3). The workability is analyzed by measuring slump, initial flow without jolting and flow with jolting, see Figure 4.3 (deviations are within 5 %).



Figure 4.3: Workability of fresh ULW-AAM: (a) slump, (b) flow without jolt, (c) flow after 15 times jolts.

Increasing the L/B ratio and the related mixture liquid content from 140 to 175 l/m³ (based on own preliminary research) strongly affected the fresh concrete performances, with the fresh mortars changing from very stiff to mixtures with self-levelling properties. At the liquid dosage of 140 l/m³ (L/B 0.28), the mortar was very stiff (zero slump), while at the 150 to 160 l/m³ (L/B 0.3-0.33) the workability was relatively high, with an initial slump ≥ 250 mm and initial flow ≥ 550 mm. This is in line with common practice and previous research, showing a workability increase when L/B ratio rises. The overall result indicates that a significant range between zero and high workability is caused by a small extra amount of liquid. This makes the ULW-AAM concrete potentially sensitive to liquid content. Furthermore, the workability in time up to 60 min strongly declines due to the high LWA liquid absorption (described in Section 5.1.1). Figure 4.4 shows the workability of recipe AAM-B-2 with 150 l/m³ of liquid direct after mixing (a) and at one hour (b). It is shown that the slump decreases significantly in one hour. Furthermore a minor detail to mention, within the ULW-AAM experiments fresh concrete temperatures varied between 20 and 24 °C and remained constant up to 60 min. The preliminary research also showed that the used AAM mineral binder produces a temperature development of up to around 40 °C. This is fairly low compared to that of normal PC based mixtures and their relatively high temperature development of \geq 60 °C.



Figure 4.4: Workability of mixture AAM-B2: (a) right after mixing, (b) one hour after mixing.

The calculated, fresh and oven-dry mixture densities are illustrated in Figure 4.5a. Deviations are within 5 %. In overall, the calculated and measured fresh concrete densities are relatively similar. The increase of fresh density in time is related to the liquid absorption of the LWA in time, as indicated by Table 4.2. This increases the LWA in mass, without changing its volume. However, the related oven-dry densities overall strongly decrease up to 15 % when more liquid is used in the mixture, caused by evaporation.



Figure 4.5: (a) Density, and (b) compressive strength of ULW-AAM versus liquid/binder ratios.

Increasing the total liquid content (or higher L/B ratio) of the mixture results in a higher water permeable porosity which negatively affects the compressive strength. As a consequence, in the experiments the strength is reduced, up to 17 %, when the liquid content increases from 140-150 l/m³ to 175 l/m³ (see Figure 4.5b). This is in line with the previous research which shows that when the L/B ratio is too high, an optimal strength development at 28-days of age is not generated [40–43]. Besides the strength, the thermal conductivity was also measured, and the results are presented in Table 4.4.

	AAM-B1	AAM-B2	AAM-B3	AAM-B4
Thermal conductivity (W/(m·K))	0.172	0.174	0.159	0.144
Water penetration (mm)	12.3	17.0	16.0	n.m.
·				

Table 4.4: ULW-AAM properties with various liquid dosages

n.m.: not measured

In overall it is illustrated that the TC decreases up to 17 % (as compressive strength) when the L/B ratio is increased. As explained, at a higher L/B, more liquid evaporates in oven-dry state which increases the voids in the concrete which favors the TC. This is also in good agreement with the previous research, stating that TC decreases at a lower density [28,44]. The overall relations between the compressive strength, thermal conductivity and L/B ratio (with 140, 150, 160 and 175 l liquid per m³ mixture, respectively) are summarized and plotted in Figure 4.6.



Figure 4.6: The compressive strength and thermal conductivity versus L/B ratio at 28 days of age.

Finally, the water penetration under pressure of the hardened ULW-AAM is tested and the results are listed in Table 4.4. In overall, the water penetration is between 12 and 17 mm, showing that the concrete is relatively low-permeable in structure even when it contains extremely high amount of porous LWA.

5.2.2 Effect of binder/aggregate ratio and LWA size

To further optimize the ULW-AAM concrete, two additional design parameters were investigated. Firstly, the binder/aggregate (B/A) ratio was studied. Decreasing the absolute binder content could reduce the TC as a consequence of the reduced concrete density. As stated, the particle density of the binder (2500 kg/m³) is \approx 6 times of the LWA (average 400 kg/m³) and this is therefore the most dominating parameter affecting the concrete porosity. Secondly, the effect of the LWA particle size was tested. Replacing the 4-8 mm LWA (crushing resistance of 1.9 MPa) by 2-4 mm LWA (crushing resistance of 2.2 MPa) may possibly further increase the ULW-AAM compressive strength.

5.2.2.1 Effect of binder/aggregate ratio

In mixtures AAM-C1-2, binders of 492 kg/m³ and in mixtures AAM-C3-4, 400 kg/m³ are used, as listed in Table 4.3. The experiments show that when applying a lower B/A ratio, the fresh concrete workability (slump and flow) significantly degrades. Applying less binder and more LWA leads to an increased amount of the liquid absorbed by the LWA. From the mixtures it is observed that with a binder reduction of \approx 25 %, the fresh density declines from 949 to 808 kg/m³ (17 %). Consequently, the 28 day compressive strength declined up to 25 % (see Figure 4.7).



Figure 4.7: Compressive strength of ULW-AAM with different binder contents or LWA fractions. Binder and LWA fraction size respectively: AAM-C1: 492 kg; 0.25-8 mm, AAM-C2: 492 kg; 0.25-4 mm, AAM-C3: 400 kg, 0.25-8 mm, AAM-C4: 400 kg, 0.25-4 mm.

A lower density causes a lower compressive strength [22,45]. Nevertheless, the lower B/A ratio significantly contributes to a decrease of the TC of the mixtures with 4.0-8.0 LWA (0.174 to 0.074 W/(m·K)) and without 4.0-8.0 LWA (0.127 to 0.070 W/(m·K)), as shown in Table 4.5).

Table 4.5: ULW-AAM properties with various binder/aggregate ratios and different LWA particle sizes fraction.

	AAM-C1	AAM-C2	AAM-C3	AAM-C4
Thermal conductivity (W/(m·K))	0.174	0.127	0.074	0.070
Water penetration (mm)	17	8.3	17.3	12.3

This is in line with the previous research, which stated that the thermal conductivity decreases from ≈ 1.75 to 0.16 W/(m·K) when lowering the density from 2300 to 400 kg/m³ [22,44,45]. Compared to the most optimal TC of ULW-PC (PC based) which was 0.12 W/(m·K) [18], the ULW-AAM illustrates a potential to generate an extremely low TC (0.070 W/(m·K)) at a moderate compressive strength of 8 MPa. Furthermore, it is observed that the water penetration under pressure is higher at a lower B/A ratio, illustrated in Table 4.5. In this case, lowering the binder content leads to a decreased material density and higher porosity, which result in a higher water permeability [46]. Nevertheless, the results are still within the acceptable range.

5.2.2.2 Effect of LWA size

In mixtures AAM-C1 and AAM-C3, LWA of 4.0-8.0 mm are applied and in mixtures AAM-C2 and AAM-C4, the 4.0-8.0 mm LWA are replaced by 2.0-4.0 mm LWA, as listed in Table 4.3. It is indicated that the workability significantly decreases when the 4-8 mm LWA are replaced by 2-4 mm LWA. This is attributed to the fact that the water demand of smaller LWA particles is higher than bigger particles, due to the increase of the specific surface area [47].

The replacement of larger particles by smaller particles has no significant effect on the calculated, fresh and oven-dry densities. Nonetheless, it positively influences the compressive strength and TC. The strength increases up to 11 % when the volume of 4-8 mm LWA is replaced by 2-4 mm LWA, see Figure 4.7. As stated, this can probably be attributed to the higher crushing resistance of the smaller particles (given in Table 4.2). The TC declines with 27 % from 0.174 to 0.127 W/(m·K) when 492 kg/m³ binder is applied (Table 4.5). This is in line with the previous research, i.e. the thermal conductivity reduces when smaller particles are applied as a consequence of the air pores (in the LWA particles) which can be distributed more homogeneously in the mixture [17]. When 400 kg/m³ binder is applied, the effect of LWA size is less prominent, with only a very slight decrease from 0.074 to 0.07 W/(m·K), Table 4.5. The TC of the mixture with 4-8 mm LWA is already almost equal to the TC of 2-4 mm LWA (0.07 W/(m·K),

Table 4.2). Therefore, it is most likely that the replacement of the LWA will positively affect the strength, while the TC remains similar. Nevertheless, it is noteworthy that here it is also observed that the TC increases (0.07 to 0.14 W/(m·K)) when an excessive amount of small particles is applied (44 instead of 8 wt. % 0.25-0.5 mm LWA and 20 instead of 63 wt. % 2-4 mm LWA, Mixtures AAM-E and AAM-C4, see Table 4.3). This indicated that a certain balance between small and big particles to achieve the lowest TC is desired.

The water penetration under pressure decreases when the smaller particles are applied, see Table 4.5 (AAM-C2 compared to AAM-C1 and AAM-C4 compared to AAM-C3). This is in line with the previous research which reported that the water permeability increases when the interconnectivity of the pores increases, which is the case when larger particles are applied [48].

5.2.3 Effect of air entraining agent

Air pockets (macro to micro air bubbles) within concrete are known as a crucial parameter to influence the density, strength and TC, i.e. the insulation potential. The influence and performance of a proper working air entraining agent (AEA) is analyzed whereby mixture AAM-D1 (promising mixture) is used as a reference. Within this recipe, an AEA with a dosage of 3 l/m³ is added (mixture AAM-D2). The density of the mixture declined with 7.7 % from 949 (AAM-D1) to 881 (AAM-D2) kg/m³ by entrapped air and increased porosity (Figure 4.8, deviations within 5 %), which is in line with the previous research [28,44,49].



Figure 4.8: Densities and compressive strengths of ULW-AAM with and without AEA.

In other words, ≈ 8 % of air is entrained in the fresh concrete. As a result, the TC decreased with 15 % compared to the reference, from 0.127 to 0.108 W/(m[·]K) (see Table 4.6), which is in agreement with previous research [22,28,44,45].

	AAM-D1	AAM-D2
Thermal conductivity (W/(m·K))	0.127	0.108
Water penetration (mm)	8.3	22.7

Table 4.6: ULW-AAM properties with and without AEA.

Despite the positive influence of the air entraining agent on the density and TC, 16 % loss of compressive strength is observed (11.5 to 9.7 MPa; Figure 4.9), which is also in line with the previous research [22,45]. The water penetration under pressure rises from 8.3 to 22.7 mm for the mixture without and with AEA (Table 4.6). In the previous research it is observed that with a lower density (which is the case in the mixture with AEA) an increase of water permeability is observed, possibly due to the capillary effect and the interconnection between air pores [46].

5.2.4 Effect of NaOH concentrations

The concentration of NaOH is of great importance affecting the AAM properties as for example compressive strength development [50,51]. Compared to the literature, in this study already a relatively low concentration of activator of 3 molar (M) is used. To analyze its influence on the performance of ULW-AAM and in addition to optimize the utilization, further lowering of the alkalinity to 2 M (AAM-E2) is tested as listed in Table 4.3.



Figure 4.9: Compressive strength of ULW-AAM with different NaOH concentrations.

Both concrete mixtures did not show clear differences between their fresh properties since both had a very poor workability (no slump). Additionally, the density, TC and water penetration under pressure were not significantly deviated. Nevertheless, the 28 day compressive strength at 2 M compared to 3 M significantly increased with 36 % from 6.6 to 9 MPa (Figure 4.9).

This is in contrast with literature, stating that the compressive strength increases towards an optimum when the NaOH molarity increases from 2-3 to 4-6 M (from 18 MPa at 3 M NaOH to 25 MPa) [51]. The strength development and polycondensation of the network is mainly affected by a number of factors, including the total element composition silicon (Si), aluminium (Al), calcium (Ca) and sodium (Na), their amorphous or mineral state and the ratio of the binder and aggregates [52,53]. As the predefined AAM binder concept used within this study has shown the most effective in strength development at 3-5 M NaOH (tested in normal density concrete mixtures based on 400 kg binder in combination with sand and gravel). The strength increase of the ULW-AAM at 2 M may be explained by the amorphous glass structure of the LWA, which is mainly composed of the elements Si and Na. These amorphous LWA will be more reactive in comparison to crystalline structured sand and gravel. If so, the extra dissolution of these elements from the LWA enhances more network growth and reaches its optimum Si:Al, SiO2:NaOH and SiO2:Na2O ratio and related higher compressive strength at a lower molarity [54,55]. It should be noted that in the preliminary research it was found that when the molarity NaOH decreases from 2 M to 1 M, the 28 day compressive strength was strongly reduced. This is most likely caused by the fact that a certain NaOH threshold concentration is needed to facilitate and activate the system, in order to develop a proper mechanical property.

5.3 Element release of raw materials

Alkali activated material network structures are mainly built out of the elements Si, Al, Ca, Na, K and Mg [45,51,56]. Their abundance and release in time results in network condensation and final structures with related material properties. The potential release of some of these elements from the used aggregates could affect the AAM network formation. The LWA chemical composition is 71 % Si, 13 % Na, 8 % Ca and 2 % Al, in combination with its amorphous structure (instead of a crystalline structured sand or gravel), could act as a mineral precursor and alkaline activator. With a cascade leaching test within a high alkaline environment (3 M NaOH solution) the element release of LWA is measured. The results are compared to other raw concrete materials; pulverized coal fly ash (PCFA), ground granulated blast furnace slag (GGBS), glass and sand, as illustrated in Figure 4.10.

Sodium could not be accurately measured due to the high content, related to the NaOH. Mainly a high release of Si is shown by the LWA and PCFA, which is much higher compared to that of glass and sand. This is most likely because both materials are mainly composed of reactive glassy silicon structures. Furthermore, LWA has a moderate release of element Al and K and almost no Ca. Although, the LWA only consist of 2 wt.% Al (23 % in PCFA), its relatively high abundance within the eluent indicates that its initial structure is relatively soluble. In overall, the results show that the alkaline environment stimulates the LWA and PCFA particle solubility and element release whereas the glass and natural sand show much lower releases. Since the mixtures AAM-E1-2 were composed of 388 kg/m³ AAM binder (i.e. 116.4 kg/m³ PCFA) and 278 kg LWA, the high amount of LWA may provide the AAM system with significant amounts Si, Al and maybe Na building block elements. The more optimal Si:Al, SiO₂:NaOH and SiO₂:Na₂O ratios are therefore possibly achieved at a lower NaOH molarity compared to ordinary AAM concrete (based on sand and gravel aggregates), as suggested in Section 5.2.4.



Figure 4.10: Element release of raw materials in alkaline environment.

Overall, it can be proposed that the matrix between solid LWA and the AAM gel network is effectively interconnected, resulting in a higher strength and an improved performance. This is supported by the idea that due to element release of the LWA or in other words dissolution of its outer surface, network formation also starts at the outer surface generating a more effective interconnection between solid particles and formed gel structures. It is worthy to mention that no negative effect on the compressive strength of the developed concrete is observed.

5.4 Overall analysis and discussions

An overall analysis of the obtained results from this study is performed by addressing the relationships between various parameters, namely density, compressive strength and TC. They are plotted and compared with available data of ultra- and lightweight PC based concretes, since no research has been reported on ultra-lightweight AAM concretes to the authors' knowledge [18,57–61].

5.4.1 Compressive strength versus density

The 28 day compressive strength versus the apparent density is plotted in Figure 4.11a. A trend is shown between both parameters, which can be described as the quantitative amount LWA in a mixture mainly influences the mixture porosity and density, affecting the related strength. When less LWA is added and replaced by the binder in the mixture (maintaining an equal volume) porosity decreases and density and related strength increases. Deviations from the trend line of Figure 4.11 a are caused by the variations in composition of the mixtures like LWA fractions and L/B ratio [40–43]. In addition, it is found that the results obtained in this study are in line with the indicated trend of lightweight concrete, obtained from data points from previous research, shown in Figure 4.11b.



Figure 4.11a: Compressive strength versus fresh density.



Figure 4.11b: Compressive strength versus oven-dry density.
5.4.2 Thermal conductivity versus density

There is a clear trend found between the TC and density which is controlled by the material density and related total binder to aggregate ratio, illustrated in Figure 4.12. A strong decline of the TC is noticed when ULW-AAM density drops. This is mainly affected by decreasing the binder content will result in a lower material density which favors an increase in porosity and a reduced TC. All data points (Figure 4.12) below the trend line are generated from mixtures with a low binder content (400 kg/m³ instead of 492 kg/m³) and/ or 2-4 mm instead of 4-8 mm fraction LWA.



Figure 4.12: Thermal conductivity versus density.

5.4.3 Thermal conductivity versus compressive strength

In line with the previous research, it is shown that the TC rises as a function of compressive strength, as illustrated in Figure 4.13 [22,45,62]. This effect on the development of the TC is less strong compared to material density, as shown in Figure 4.12. The reduction of TC is mostly affected by two parameters; primarily by a reduced binder content or so-called binder/LWA ratio (400 instead of 492 kg/m³ binder in a mixture), and secondly to a lower extent by the use of LWA faction and replacement of 4-8 mm by 2-4 mm LWA.



Figure 4.13a: Thermal conductivity versus compressive strength of ULW-AAM.



Figure 4.13b: Thermal conductivity versus compressive strength of ULW-AAM and other concrete data obtained from literature.

Additionally, the obtained TCs from the ULW-AAM are significantly lower (at an equal compressive strength level) compared to the other PC based concrete from the literature, as illustrated in Figure 4.13b. This can be partly explained by the used raw materials and their properties. Firstly, the LWA used in this study and in the study of ULW-PC is low in density and relatively high in crushing resistance. For example the aggregates applied in the literature are expanded glass and foam having a lower crushing resistance [59,60] or expanded clay with a higher density [57]. Furthermore, some of the ULW-AAM mixtures produced a significantly lower TC compared to the reference ULW-PC, even when a comparable binder content was used [18]. This difference can be explained by that a reduction in TC is reached when part of the PC binder was replaced by fly

ash or blast furnace slag. The reduction of the binder density is the main reason for the decreased TC [63]. In addition, compared to PC these binders are significantly lower in Ca and higher in Si and due to their amorphous structure, a lower thermal conductivity is obtained [63]. Related to the AAM binder within the ULW-AAM (composed out of PCFA and GGBS), this could be a possible explanation for the lower TC of the ULW-AAM compared to that of the ULW-PC [44,63].

5.4.4 Comparison with other building materials

The designed ULW-AAM showed very promising thermal properties compared to other traditional building materials, especially at a comparable strength class. For example, ordinary concrete with a compressive strength ≤ 40 MPa has a high TC of around 1.7 W/(m·K) [64]. ULW-PC has a TC of 0.12 W/(m·K) at a strength of 10 MPa [18]. Cement based wood wool boards have a TC of 0.08 W/(m·K), however are not designed for load bearing purposes. Stone wool and glass wool products have a TC of respectively 0.035 and 0.040 W/(m·K), respectively, which however are also not designed for load bearing purposes [65,66]. This highlights the excellent properties of ULW-AAM with a TC of 0.07 W/(m·K) and a 28 days compressive strength of 8 MPa.

6 Conclusions

This chapter addresses the design, production and performance evaluation of ultralightweight alkali activated concrete (ULW-AAM), a potential load bearing and thermal insulating building material. The applied AAM system has, compared to PC and other AAM binders, superiorities in terms of sustainability, favored by the use of the industrial by-products mineral as binder raw materials and relatively low NaOH activator molarity (2-3 M). With a compressive strength of 10 MPa, a very low thermal conductivity of 0.108 W/(m·K) is resulted by the developed ULW-AAM, and the thermal conductivity even further reduces to 0.074 W/(m·K) at a compressive strength of 8 MPa. By understanding the influences of all the controlling parameters and related material properties, a fully optimized and highly effective product is resulted. Based on the performed study, the following conclusions are reached:

- *Mixture design approach:* mixtures designed applying an optimized packing approach gain improved mixture stability and workability with an effective porosity and lower TC.
- *Liquid/binder (L/B) ratio:* increased liquid dosage (140 to 175 l/m³) and related higher L/B ratio affect the workability significantly (slump from 10 to 280 mm) and lower the oven-dry density, 28 day compressive strength and TC with 15-17 %, due to the increased porosity.

- *Binder/aggregate (B/A) ratio:* the B/A ratio greatly influences the fresh and hardened ULW-AAM performance. A higher ratio increases the 28 day compressive strength (up to 25 %) and lowers the water penetration under pressure. Nevertheless, both fresh density and TC increase up to 17 % and 58 %, respectively.
- *LWA particle size:* when LWA of 4-8 mm are replaced by LWA of 2-4 mm, the ULW-AAM performance is mainly positively affected. The 28 day compressive strength increases (up to 11 %) and TC decreases (up to 27 %).
- *Air entraining agent (AEA):* the introduction of an AEA optimizes the mixture performance by further lowering the density (7.7 %) and TC (15 %). This is initiated by the created micro air bubbles. Nevertheless, a 16 % loss of compressive strength is observed.
- *Alkali activator concentration:* A higher compressive strength (36 %) of ULW-AAM is generated by lowering the alkali concentration from 3 to 2 M.
- *Element release of LWA: w*ithin an alkaline environment, a certain element release from the applied LWA is shown, mainly Si and in lesser extent Al and K as network building element. Nevertheless, the effect on the compressive strength of the concrete is negligible.

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CHAPTER 5

Leaching of oxyanions from monolithic and granular slag-fly ash alkali activated materials as a function of the mixture composition*

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Graphical abstract

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Abstract

This chapter explores the leaching of oxyanions (arsenic, molybdenum, selenium, vanadium, chromium) from slag-fly ash alkali activated materials, dependent on various mixture parameters i.e., activator molarity, slag and fly ash binder compositions, binder content, liquid to binder ratio, curing time and strength. The analyses focusses on the environmental impact of potential toxic element leaching in a monolithic and granular material state. Typically, oxyanionic species show a relatively high leaching potential and are not effectively bound as a result of the amorphous microstructure of alkali activated materials (AAM). Leaching of monolithic state AAM materials (concrete) is far below the regulatory leaching limit values even though they strongly differ in mixture composition. Within granular state AAM materials (aggregate) the NaOH activator alkalinity and the GGBS-PCFA binder content significantly influence the oxyanion leaching behavior. The release of As and V strongly increases with a higher activator molarity as an effect of changes in the pH of the system. The release of As, Mo, Se and V increases with higher PCFA content of the GGBS-PCFA binder composition. Overall, leaching of AAM aggregate meets the Dutch leaching limits for open application of granular building materials when the PCFA content within the total binder composition remains below 30 wt.%. Further, pH dependent leaching of AAM aggregate is assessed to simulate pH lowering due to potential carbonation processes.

Keywords: alkali-activated material; pulverized coal fly ash; ground granulate blast furnace slag; oxyanion metals; leaching;

1 Introduction

Alkali activated slag-fly ash binder systems and related materials (AAM) are currently seen as a partial alternative to traditional Portland cements (PC) and related concrete products [1,2]. Next to the technical performance, AAM products also have to be tested for environmental properties such as element leaching. In the Netherlands, leaching is regulated by the Soil Quality Decree [3], for monolithic (e.g. concrete) and granular (aggregate) state building materials. AAM often contain secondary mineral alkaline byproducts or waste materials (slag and ashes), such as pulverized coal fly ash (PCFA) and ground granulated blast furnace slag (GGBS) as precursors. Apart from their binder and filler function, these secondary minerals could contain variable amounts of potentially toxic heavy metals and therefore specific attention should be addressed to their leaching behavior.

Studies mainly focus on the leaching of cationic metal species such as lead, zinc, copper and barium [4-8], while oxyanionic metals (e.g., arsenic (As), selenium (Se), molybdenum (Mo), vanadium (V) and chromium (Cr)) have received little attention. Nevertheless, alkaline minerals (slags and ashes) generally have a relatively high release of oxyanion metals [9]. In this study, specifically the elements As, Se, Mo, V and Cr were selected, representing oxyanions in slags and fly ashes that could exhibit leachable concentrations from concrete and/or aggregate that might become critical with respect to the SQD leaching limits. Their leaching behavior is strongly related to their typical oxyanionic redox states [10-13] and predominantly PCFA releases significant concentrations of As, Se, Mo, V and to a lesser extent Cr in comparison with GGBS, which leaches mainly V. Little is known about GGBS leaching instead, for PCFA (class F type) distinct trends are obtained from the literature [14], showing that smaller size particles increasingly contain a higher metal (As, Mo, Se, V and Cr) bulk content and in addition the bulk content strongly correlates with the leachable concentration. Also, oxyanionic metals are mainly condensed at the outer fly ash particle surface, making them potentially easily soluble [15,16] and in particular in a (highly) alkaline environment (i.e., AAM and PC system). Therefore, in view of the mentioned PCFA and GGBS characteristics, the leaching of PCFA dominated binder systems is likely to be more significant in comparison to that of GGBS related systems [17].

Portland cement (PC) shows a relatively high oxyanion adsorption potential, although within AAM the adsorption tends to be less effective and this difference is mainly controlled by the crystalline and amorphous microstructure and related pH of both systems. From PC products low leachable concentrations are observed, as oxyanion species are mainly adsorbed within crystalline ettringite and, to a lesser extent, in calcium silicate hydrate (C-S-H) structures [17–19]. However, metal release can significantly increase when the pH of a concrete and/or aggregate lowers toward < pH 11 as an effect of concrete carbonation [20], which results in for instance the dissolution of ettringite

[21] and therefore increases the release of oxyanions such as chromium, antimony, vanadium and sulfate [19,20,22].

Within slag-fly ash based AAM the amount of crystalline structures is very low or absent since these systems are mainly composed of intermixes of amorphous M⁺ Alumino-Silicate Hydrate gels also known as CASH and NASH (M⁺: calcium, sodium, magnesium) [23–25]. These structures have less effective oxyanion adsorption properties than structures within PC, resulting in a higher oxyanion solubility and leaching potential. Additionally, the oxyanion release and adsorption behavior of C-(N)-A-S-H gel-structures is less well studied. Geochemical modeling indicates that reduced oxyanion solubility occurs in alkaline systems where (calcium and iron) metalate precipitates are formed under the influence of pH; it is mainly the leaching of calcium and iron through dissolution, adsorption and precipitation reactions which could be of influence [10]. Overall, this implies that mainly PCFA and GGBS as precursors and related element content and release in combination with the alkaline content, are of strong influence to metal leaching, as these parameters finally determine the specific dominated AAM microstructure composition. In addition, leaching is influenced by other physical/ chemical mixture parameters such as pH, liquid to binder ratio, binder content, curing time and material strength.

Therefore an improved understanding of the release controlling factors is needed to be able to design AAM mixtures and related products and to control and predict their leaching of oxyanions. This understanding is of importance during the intended use of the products (monolithic state), nevertheless also at the end of the AAM concrete service life as granular (aggregate) building materials. In the aggregate phase, the initial high alkaline pH value will gradually proceed to more neutral pH, typically pH 8-9, due to carbonation [22,26]. These chemical changes have a significant effect on anion leaching of AAM in a granular and/or its second life (aggregate) state [22,26–28]. In order to manage this material using an environmental and safe approach consistent with the common practice of traditional concrete recycling, the objectives of this study are:

- Characterize the oxyanion metal content and release of single PCFA and GGBS at the natural alkaline conditions.
- Investigate the leaching of monolithic state (concrete) and granular state (aggregate) AAM as a function of the mixture composition that differs in: activator molarity, PCFA and GGBS binder composition, binder content, liquid to binder ratio and sample age and strength.
- Correlate and predict the leaching of AAM aggregate as a function of the slag-fly ash binder content.
- Examine the influence of the pH on metal leaching, mechanism and behavior from the single PCFA and GGBS, and AAM. To provide information on the leaching properties of AAM in the recycling stage after use as a fresh and carbonated aggregate. In this

respect, a comparison is also made to the pH dependent leaching properties of regular blended Portland cement materials containing fly ash and/or blast furnace slags.

2 Materials

The following precursors were used: 3 different class F type pulverized coal fly ashes in accordance with NEN-EN 450 produced in the Netherlands and Germany and a standard quality ground granulated blast furnace slag (GGBS). A technical grade sodium meta-silicate pentahydrate powder (supplied by PQ), was applied in the mixture. Further Industrial grade liquid sodium hydroxide (NaOH) was used to prepare the activator solution and had an initial 11.2 molarity (M). This stock solution was diluted with demineralized water to the desired molarity needed within the mixture designs. A polycarboxylate plasticizing admixture hereafter identified as 'admixture' was used to optimize the fresh concrete workability (supplied by SQAPE Technology). For mortar sample production, oven dried (24 hours at 80°C) natural 0-4 mm sand was applied. The relevant material properties are listed in Table 5.1

Material	Specific density (kg/L)	*Water demand (ml)	PSD d50 (µm)
PCFA-1	2.293	29	22
PCFA-2	2.334	27	24
PCFA-3	2.268	29	25
GGBS	2.893	39	12
Sand 0-4 mm	2.611		
Meta silicate powder	900		650 till 900
NaOH solution 11.2 M	1.360		

Table 5.1: Material properties.

PSD: Particle Size Distribution

3 Design and methodology

Firstly, the leaching of single PCFA and GGBS was analyzed within different aqueous solutions from neutral to highly alkaline conditions to investigate As, Mo, Se, V and Cr leaching as a function of solution alkalinity.

Secondly, alkali activated GGBS-PCFA mortar mixtures were prepared that vary in (1) NaOH concentration, (2) the GGBS-PCFA mass proportion of the total binder composition, (3) the liquid to binder (L/B) ratio and (4) sample curing time. This was done to investigate the effects of changing mixture composition on the compressive strength developed and the leaching of oxyanion metals. The testing of sample curing age (7 till 91 days) in relation to strength and leaching is performed on an average mortar mixture D1. The detailed mixture compositions are presented in Table 5.2. All mixtures were composed with 3 M NaOH, apart from mixtures A1-A5. Preliminary study and the literature [29-31] indicated that strength as a function of the NaOH content has an optimum at around 3 to 4 M NaOH.

Thirdly, results are presented for the total element leaching of monolithic state AAM concrete mixtures. This is also done for the leachability of critical oxyanion metals of granular state AAM material as a function of the GGBS-PCFA mass ratio of the binder composition.

Fourthly, pH-static batch leaching experiments of single PCFA and GGBS suspensions and of a 28-day-old AAM mortar mixture were carried out. The tested AAM sample is mixture B3 of Table 5.2 (binder composition: 375 g of PCFA and 125 g of GGBS), which is an average and well performing AAM mixture in comparison to all tested mortar designs. The experiments describe element release behavior of As, Mo, V, Se and Cr of the initial binder minerals in relation to the hardened AAM as a function of pH ranging between pH 2 to 13. Additionally, this data is plotted together with the leaching results of blended (GGBS and/or PCFA) Portland cements mixtures, i.e., CEM II/ CEM III/ CEM V, obtained from previous studies [19,32,33] as to compare the leaching potential between both AAM and Portland cement binder systems.

The mortar preparation and experiments shown in Table 5.2 was mainly based on standard NEN-EN 197.1, with exception of the prescribed 0.5 liquid to binder (L/B) ratio, which was lowered due to the initial lower precursor liquid demand. Mortar mixtures were prepared using a Hobart mixer, all materials, e.g., sand, PCFA-2, GGBS, silicate powder and liquid, were added in one single step with a total mixing time of 3 minutes. Within mixture preparation the water, NaOH and admixture was addressed as the total liquid volume (although it contains some solids). After mixing, the fresh mortar was cast in polystyrene prism molds (40 x 40 x 160 mm³), finished with a compaction table and sealed with plastic foil to prevent evaporation. Samples were stored to cure at $\approx 20^{\circ}$ C and ≥ 95 % RH, until reaching the desired age for further characterization.

Mixture	Sand	PCFA	GGBS	Total liquid	L/B	Admixture	NaOH	Na ₂ SiO ₃	Parameter
	(g)	(g)	(g)	(ml)	ratio	(g)	(M)	(M)	variation
A1-A5	1350	325	125	160	0.36	3	<u>1 - 5</u>	0.125	1 M
B1-B4	1350	<u> 375 - 300</u>	<u>75 - 150</u>	160	0.36	3	3	0.125	25 g
C1-C4	1350	325	125	<u>140 - 200</u>	<u>0.31 - 0.44</u>	3	3	0.125	20 ml
D1	1350	325	125	160	0.36	3	3	0.125	

Table 5.2: Mortar mixture composition.

Bold and underlined indicate changed parameters.

4 Experiments methods

Compressive strength measurements of mortar samples were performed in-time at the age 7, 91 days in accordance with NEN-EN 196.1.

Batch leaching experiments in accordance with NEN-EN 12457-2, "compliance test for granular samples" [46], were done on single PCFA and GGBS suspension samples. A lower L/S ratio (51/kg) was used instead of the standard L/S 10 in order to generate higher concentrations that can be more precisely determined. PCFA is known to release higher oxyanion concentrations with a higher deviation in comparison to GGBS, therefore three different ashes were tested. A total of 40 g material was mixed with 200 ml of demineralized water and/or 3M NaOH solution with a liquid to solid (L/S) ratio of 5. The suspension was shaken for 24 h before filtration over 0.45 μ m membrane filter. In total, 40 ml eluate was acidified with 9 ml 70 % pure nitric acid, to a pH \leq 2. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used for element analysis.

Additionally, batch leaching experiments, in accordance with NEN-EN 12457-2, on hardened AAM samples were done after crushing the materials to ≤ 4 mm. A total of 20 g crushed material was mixed with 200 ml of demineralized water with L/S 10. Similarly, as described above, the suspension was shaken for 24 hours before filtration over 0.45 μ m membrane filter and then eluates were acidified to a pH ≤ 2 before element analysis with ICP-AES.

Batch pH-static leaching experiments were carried out on granular material in accordance with EN 14997 to determine element release as a function of leachate pH of (1) single GGBS and PCFA powder samples and (2) 28-day-old hardened AAM mortar samples (after crushing the materials < 4 mm). The subsamples were subjected to leaching at L/S 10 L/kg and were continuously stirred for an equilibration time of 48 hours, at predetermined pH values between 2 and 13.5. The pH of the different suspensions was controlled using solutions of 1 M HNO₃ and NaOH (analytical grade) and a computerized pH-stat system. After the equilibration, the suspension was filtered

through 0.45 μm membrane filter and the eluate was acidified with concentrated HNO_3 and analyzed by ICP-AES.

The tank leaching test in accordance with NEN 7375 was performed on concrete mixtures at 28 days of age "compliance test for monolithic samples". Chemical analysis of leachates from leaching tests was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Chloride (Cl), bromide (Br) and sulfate (SO₄) were analyzed using ion chromatography (IC). Fluoride was analyzed by flow injection analyses with spectroscopic detection.

5 Results and Discussions

5.1 Leaching of PCFA and GGBS in high alkaline conditions

Table 5.3 shows the chemical compositions of the different class F type fly ashes and a GGBS, which is in good agreement with the literature [17,34]. GGBS is very low in oxyanion metal content while PCFA contains higher quantities. Additionally, oxyanion leaching of PCFA-1 to 3 and of GGBS in water (low) and 3 M NaOH (high) alkaline suspension are shown in Tables 5.4 a and 5.4b, respectively.

For GGBS in a water suspension, all measured oxyanion concentrations are close to or below the detection limit. However, the 3 M NaOH alkaline suspension (Table 5.4b) caused a substantial increase in concentrations, although the absolute values of As, Cr and Mo are still relatively low (< 0.2 mg.kg dm). Typically the Se and V concentrations were more elevated and, in comparison with a water suspension, they were a factor 9 and 48 higher, respectively.

For PCFA in a water suspension (Table 5.4a), in comparison to GGBS, oxyanion concentrations are more significant. Leaching behavior is most certainly controlled by the pH, as results show a lower oxyanion release with a higher pH, from pH ≈ 11 (PCFA-2/3) towards \approx 12 (PCFA-1). It is characteristic that with a higher pH, starting from 11 to 12, certain cementitious structures (typically ettringite) are formed [15,35], which incorporate or bind oxyanions within their structures [36]. In the highly alkaline 3M NaOH suspension (pH 14, Table 5.4b), the release of As, Se, V and Cr from PCFA significantly rises in comparison with the water suspension. This observation is in agreement with the literature [15,33,37] and the observed pH dependent leaching results reported in Section 5.5, where in additional more detail of related mechanisms is described. The variation of the leachable concentrations between the ashes could be affected by the differences in their applied incineration processes and the initial coal type composition. In comparison with the water suspension, concentrations of As, Cr, Se, and V increased respectively by a factor of 150, 2, 5, and 24. However, the Mo concentration remains approximately at the same level, regardless of the solution alkalinity or pH. Most probably, the abundant Mo hexavalent (6+) state tends to be very chemically stable within PCFA and its leachates [10,15], which results in stable release over a wide pH ranging from 6 to 14. Also, this observed mechanism is further illustrated in Section 5.5. Chromium release from PCFA occurs likely in the form of Cr(VI), instead of Cr(III) which is chemically stable and has low solubility [38]. In addition, the observed concentrations are in-line with the literature [13,15]. Finally, all the measured oxyanion concentrations in the water and or alkaline suspensions were far lower than their initial chemical content for both PCFA and GGBS, indicating that only a relatively small amount of the abundant oxyanion content form soluble constituents.

Element		Material			
		PCFA-1	PCFA-2	PCFA-3	GGBS
Si	wt.%	54.50	52.30	51.10	34.10
Al	wt.%	24.51	25.92	23.45	9.90
Ca	wt.%	4.20	2.40	2.50	41.80
Mg	wt.%	1.25	0.98	1.28	7.70
Fe	wt.%	7.40	9.10	12.70	0.48
Na	wt.%	0.74	1.01	0.87	0.00
Κ	wt.%	2.00	2.68	3.01	0.53
Mn	wt.%	0.04	0.03	0.03	0.34
Ti	wt.%	1.15	1.08	1.02	1.20
V	ppm	420	670	700	45
Se	ppm	20	20	30	6
As	ppm	20	20	20	nd
Mo	ppm	50	70	70	nd
Sb	ppm	nd	nd	nd	nd
Cr	ppm	260	300	330	34
Sn	ppm	240	230	250	nd
Sr	ppm	1140	780	430	662
Pb	ppm	100	200	260	nd
Zn	ppm	220	330	570	13
Cu	ppm	110	210	210	nd
Ni	ppm	150	250	260	nd
Со	ppm	nd	nd	nd	nd
Ba	ppm	1430	1430	960	742
Р	ppm	5290	3010	1740	nd
LOI (950 °C)		3.9	1.5	2.5	0.0

Table 5.3: Chemical composition (measured as oxide) of mineral precursors.

nd: not detectable

Material	PCFA-1	PCFA-2	PCFA-3	GGBS
рН	12.20	11.15	11.45	11.80
As	0.06	0.16	0.23	0.02
Cr	2.53	2.60	1.46	0.05
Мо	12.00	19.00	18.10	0.004
Se	0.79	2.00	3.36	0.07
V	0.15	2.43	1.75	0.05

Table 5.4a: Leaching of PCFA and GGBS in water.

All values in mg.kg dm. Leaching determined in accordance with the batch leaching test NEN-EN 12457-3 with a L/S 5.

Material	PCFA-1	PCFA-2	PCFA-3	GGBS
pН	14.0	14.0	14.0	14.0
As	20.60	24.00	25.70	0.18
Cr	5.75	5.29	2.89	0.10
Mo	15.10	18.50	20.00	0.047
Se	11.70	10.20	14.20	0.61
V	35.50	40.60	33.10	2.38

Table 5.4b: Leaching of PCFA and GGBS in 3 M NaOH alkaline liquid.

All values in mg.kg dm. Leaching determined in accordance with the batch leaching test NEN-EN 12457-3 with a L/S 5.

5.2 Compressive strength of mortar mixtures

The compressive strength development of the AAM mortar mixtures A to D (described in Table 5.2) are shown in Figure 5.1. All mixtures show an increasing strength over time, with a 28-days strength ranging from 30 to 50 MPa. The performance is relatively good in comparison with the performance of traditional Portland cement (CEM I 42.5) and with blended Portland cements, e.g., fly ash cements (CEM II 32.5 or 42.5), blast furnace slag cements (CEM III 32.5 or 42.5), and composite cements (CEM V 32.5). Within the tested mixtures, strength as a function of the activator alkalinity (Figure 5.1a) shows to have a plateau at 3 to 4 M NaOH, which is in agreement with the literature [29–31]. Previous studies displayed similar strength stabilizing or plateau effects using a NaOH activator [31,39]. Most probably, this relatively early age strength behavior is related to the fixed reactive GGBS binder content, which dominates the microstructure development and related material hardening within the first 28 days of age. Figure 5.1b indicates a significantly higher strength when a higher GGBS particles and their high

calcium content are of significant importance in enhancing the development of the AAM microstructure and related material performance.

The strength development as a function of the liquid to binder (L/B) ratio is shown in Figure 5.1c and shows a declining trend with an increasing L/B ratio of 0.31 to 0.44. An adjustment or an increasing L/B ratio is known to affect the AAM material properties, e.g., porosity, resulting in lowering of the strength [42,43].

The strength development as a function of time (material curing age) was also assessed for a longer period than the normal 28 days period (Figure 5.1d). This Figure shows a curve that is in-line with normal hydraulic cementitious materials, namely gaining most of its strength within the first 28-dayss of hardening, which, more or less, stabilizes over time. Strength growth is assumed to be controlled by the pozzolanic behavior at a high PCFA binder content and further densification of the matrix [40,44]. PCFA begins to react significantly, densifying the matrix within a period of the first 28 to 91 days after initial mixing [45–47].

5.3 Leaching of granular and monolith state AAM concretes and mortars

5.3.1 Monolithic state leaching of AAM concrete

To assess the 'potential' hazardous element leaching of monolithic state AAM concrete and or construction materials, two samples (data obtained within preliminary study) were tested using the diffusion (tank) test. The two tested AAM concrete mixture compositions (both contain an equal admixture content) are shown in Table 5.5 although, strongly differ in composition with respect to: the GGBS-PCFA mass ratio of the total binder, NaOH concentration and L/B ratio. The main differences are that AAM-1 is high in PCFA and alkali content and AAM-2 is low in PCFA and alkali content. The 28-dayage compressive strength of AAM-1 was 45-50 MPa and AAM-2 was 55-60 MPa. This obtained strength level of both concretes is in-line with a C40/50 and C50/60 concrete strength, which is most commonly used in practice. The higher strength development of AAM-2 is related to its significant higher GGBS content, this is in agreement with data of Figure 5.1b and with the literature [40].

Measured element leaching in comparison with the leaching limit values regulated by the Dutch SQD [3] for monolithic construction materials are shown in Table 5.6. The results show that all measured leaching values for both samples are far below their regulatory limit values for monolithic construction materials. Further, it can be clearly observed that, due to the higher PCFA binder content and NaOH content of sample AAM-1, a higher oxyanion release of Sb, As, Mo, Se, V and Cr is a typical result. A possible explanation for this effect is the higher system alkalinity affected by NaOH and higher oxyanion content in the system affected by a high PCFA content. Fly ash contains and generates a much higher oxyanion leaching potential in comparison to GGBS, as observed by the results of Section 5.1.





	AAM-1	AAM-2
Binder content (kg/m³)	450	350
Sand 0-4 mm (wt.%)	≈ 50	≈ 50
Gravel 4-16 mm (wt.%)	≈ 50	≈ 50
Binder composition		
PCFA (wt.%)	75	25
GGBS (wt.%)	25	75
NaOH (M)	± 5	± 3
L/B ratio	0.29	0.42

Table 5.6: Element release of monolithic state 28 days old AAM concretes in comparison with th	e
SQD limits for monolithic building materials, measured with the diffusion test in accordance wit	h
NEN 7375.	

Parameter	AAM-1	AAM-2	Limit monolithic material
pH start	10.7	11.2	no limit
pH end	11.8	10.6	no limit
Sb	1.8	0.4	8.7
As	50.2	2.1	260
Ba	0.7	10.2	1,500
Cd	0.1	0.1	3.8
Cr	1.5	1.0	120
Со	0.2	3.0	60
Cu	0.6	2.0	98
Hg	n.m.	0.04	1.4
Pb	0.8	5.0	400
Mo	28.3	1.0	144
Ni	0.4	5.0	81
Se	2.6	0.8	4.8
Sn	0.6	3.0	50
V	70.3	3.2	320
Zn	1.6	5.0	800
E	01	74	2500
F Cl	01	/4	110000
CI	13/	12/	110000
SO ₄	9409	1429	165000
Br	94	20	670

All units in mg/m²/ 64 days.

n.m.: not measured

5.3.2 Granular state leaching

When monolithic state AAM concrete and/or constructions eventually come to the end of their service life, these materials are mostly demolished and the size reduced into aggregates. To assess the environmental properties of these materials at the "end of life" stage, it is therefore important to assess the leaching at the granular stage. Oxyanion metal leaching of 28 day old mortar mixtures (described in Table 5.2), that are size reduced up to < 4 mm granular material, is shown in Figure 5.2. The related compressive strength data of the tested mixture is shown in Figure 5.1. The linear correlations plotted in Figures 5.2a, b, c, are only intended to clearly present the relation between element leaching as a function of a varying NaOH concentration, binder compositions, and L/B ratio within the tested mixtures.

Figure 5.2a shows the metal leaching of granular AAM as a function of system alkalinity. For V and As, concentrations linearly increase with a higher NaOH molarity and related higher pH. The release of Mo and Se is relatively stable over the total NaOH range, indicating both elements are highly soluble in an alkaline system and already reach their maximum and/or equilibrium concentration at 1 M NaOH alkalinity. The release of Cr decreases with a higher NaOH content; no clear explanation of this effects can be given. Figure 5.2b presents the metal release of granular AAM as a function of the PCFA content within the total binder. All the metal concentrations with exception of Cr, increase with a linear correlation, because of a higher PCFA binder content. Which can be explained by metal release in AAM mainly originates from PCFA as it contains, in comparison to GGBS, a significantly higher metal content relates to a lowering of oxyanion stabilization of metalates [41]. Assuming that (Ca and Fe) metalate precipitates from GGBS in alkaline systems, the oxyanion leachate concentrations are reduced [10] (further discussed in Section 5.5).

Figure 5.2c describes the leaching of granular AAM as a function of the mixture L/B ratio. For As and V, the release increases proportional to a higher L/B. Leachability of Mo, Se and Cr tends to be more stable over the total L/B range.

Figure 5.2d illustrates the metal release of granular AAM as function of sample curing time (days). No clear trends are observed between leaching and curing time and/ or related strength other than an initial effect, which occurs within the first two weeks. All oxyanion concentrations clearly increase up to 14 days of curing, most probably as an effect of continuous progress of particle dissolution or corrosion under influence of alkali. Further in time, oxyanion concentrations stabilize as particle dissolution and related microstructure development diminishes.





5.4 Oxyanion leaching versus slag-fly ash binder composition

It was observed that the precursor/binder composition (Figure 5.2b) and typically the PCFA content is of significance to the oxyanion release. Therefore, the leaching of the granular state AAM material was also estimated as a function the GGBS-PCFAS precursor composition. This approach could be helpful to estimate the leaching of 'future' AAM aggregate in comparison with the leaching limit values defined within the Dutch SQD [3] for the application of open granular building materials. Figure 5.3 presents the leaching of V, As, Se, Mo and Cr as a function of the PCFA mass in the total binder of 28-days-old granular AAM material. Note: the AAM mortar data represents the mixtures B1 to B4, described in Table 5.2. The added AAM concrete data is obtained from previous study and is shown for comparison and as a supplement within the presented trend lines. The data of both mortar and concrete mixtures do not show completely similar element leaching behavior. Their difference in mixture L/B ratio, mortar (0.36) and concrete (0.47), could also be of influence to their observed leaching behavior.

Apart from the individual paste and concrete trend lines a black dotted trend line is plotted representing the fit of both data sets, showing an indicative and/or prediction of the leaching behavior. Clearly the measured release of all oxyanions is explained by a declining trend as a function of lower PCFA content, i.e., V, As, Mo and Se are explained by a declining curve (explained with a power trend). Chromium leaching declines with a linear trend as function of a lower PCFA content, although this effect is less significant due to its relatively low measured concentration. For Mo, the release is almost a direct function of the PCFA content and it is not released by GGBS. This observation is in agreement with data of Tables 5.4a, b, showing Mo is chemically very stable within PCFA and its leachate; favoring a high and stable solubility from an alkaline mineral and within low to high alkaline pH environments [10,15]; and with data of the pH dependent results (further discussed in Section 5.5). Overall, the black dotted prediction trend lines indicate that a GGBS-PCFA binder composition with roughly up to 30 wt.% of PCFA is needed to meet the SQD leaching limits for open application of granular AAM building materials. This deducted PCFA content is mainly determined by the leaching of Se, which is critical to the leaching limit value even at low PCFA content.





Apart from the influence of the binder composition of leaching, it was assessed how the binder content (at one chosen binder composition, ≈ 75 wt.% GGBS and ≈ 25 .wt.% PCFA) affects the leaching of oxyanions. Figure 5.4 shows the leaching of V, As, Se, Mo and Cr of 28-days-old granular AAM material (aggregate) obtained from concrete mixtures using a different binder content (300-500 kg/m³).The results show that if the total binder composition (wt.% of PCFA and GGBS) remains constant, an increase in binder content (kg/m³) in AAM concrete will not largely affect the leaching (behavior and concentration) of the obtained granular state material. Apparently, the fixed precursor composition maintains the potential to influence the adsorption or release of oxyanions, also at higher binder content.



Figure 5.4: Leaching of vanadium, arsenic, selenium, molybdenum and chromium as a function of the binder content of 28 day old laboratory produced AAM concrete. Data from preliminary research measured on granular \leq 4 mm material, conform NEN-EN 12457-3. Concrete mixture compositions; 43 wt. % sand 0-4 mm and 57 wt. % gravel 4-16 mm, \approx 3 M NaOH, a fixed \approx 25 wt.% PCFA and \approx 75 wt.% GGBS binder composition and a varying 300-400-500 kg/m³ binder content. All sample pH's ranges between pH 12.1 to 12.3.

The results showed equal concentration heights of As, V, Se and Cr, independent of the binder content. With exception of Mo release, which slightly decreases from 0.78, 0.62 to 0.53 mg.kg dm with a higher binder content. This effect directly corresponds with the applied mixture L/B ratio. Where the L/B ratio decreases from 0.40, 0.34 and 0.32 within the mixtures with a higher 300, 400, 500 kg/m³ binder content.

5.5 pH dependent leaching dynamics of AAM and precursors

Results of the pH dependence leaching test are used to evaluate the leaching properties of AAM in granular state under fresh and aged conditions, which is mainly reflected in a difference in material pH. Figures 5.5 and 5.6 present the leaching of V, As, Se, Mo, Cr and Si, Al, Ca and S, respectively, of the single precursors PCFA and GGBS and an AAM

mortar (after 28-days of curing). The concentrations are expressed in mg.kg (at L/S 10) analogous to the SQD regulations, allowing to make a comparison (although normally, the percolation test is performed for a comparison with the limit values). The initial or own pH of all shown materials is around pH 12-12.5, which is representative for the fresh material in granular state after crushing into aggregates. For granular materials, pH \approx 8-9 is representative at its final leaching, as the initial pH gradually declines due to carbonation processes as a function of time [22,26].

Compared to PCFA, the GGBS exhibits low oxyanion release over the entire pH range, which is in-line with data of Tables 5.4a, b and is therefore not responsible for the considerably higher leaching of the AAM. The pH dependent leaching patterns (Figure 5.5) of Se, Mo and Cr from PCFA are similar to those from the AAM, indicating that similar geochemical processes control leaching. In particular, Se and Mo are characterized by a horizontal (pH independent) pattern indicating a virtually complete dissolution of their available amount. Both V and As (Figure 5.5) show a pH dependency which is quite different from AAM, and even exceed that of AAM around its own pH 12, indicating that distinctly different geochemical processes control leaching between the PCFA precursor and the AAM. This observation differs from the use of PCFA in regular Portland cementitious materials as different combinations of fly ash sources and usage rates do not increase the leaching to levels greater than typical ranges for cement materials not containing PCFA [32,33]. This is further illustrated (Figure 5.5) by the added 5% and 95% percentiles of PCFA and GGBS blended Portland cement mixtures from previous studies [19,32,33]. In regular Portland cementitious materials oxyanions show a decreased leaching above pH \approx 11, which is associated with the formation of ettringite, which acts as a sink for trace oxyanions replacing sulfate [18,21,27].

The leaching of calcium from AAM is orders of magnitude lower than in regular blended Portland cements (Figure 5.6). On the other hand, the leaching of Si, Al and sulfur (S) from AAM at the natural pH (pH 12.5) is substantially higher than the observed range for Portland cement. The low content and solubility of Ca and the corresponding high solubility of Al and S, seem to indicate that ettringite, the natural "sink" for oxyanions at high pH in regular cementitious materials, is not formed in this AAM system. Ettringite absence also explains the invariant (Se, Mo) or continuously increasing leaching of (V, As, Cr) oxyanions between pH 10 and 13.

The pH dependent leaching trends for V, As, Se, Mo and Cr (Figure 5.5) all show typical anionic behavior. This behavior follows the pattern characteristic for the adsorption to iron (hydr)oxides [27,48] i.e., an adsorption maximum at low pH (V, As, Cr at pH 5; Mo at pH 3; Se does not show a clear adsorption maximum), and negligible adsorption at high pH. Previously, using geochemical modelling, similar pH dependent leaching trends for Mo, Cr and V where observed in recycled concrete aggregates as explained by iron (hydr)oxide sorption, [23]. The differences in pH dependent leaching trends and location of the adsorption maximum generally reflect their different affinity for binding

to the iron (hydr)oxide surfaces and solution speciation, but are also influenced by competition between anions for a limited amount of surface sites [48]. Furthermore, As and V have, by far, the highest Fe-adsorption affinity and their leaching behavior indicate continued desorption (higher release) after their adsorption maximum of around pH 5, up to high pH values (Figure 5.5). A relatively weak Fe-adsorption potential is observed for Mo and Se and, in particular Se and Mo above pH 5, show complete desorption over the full pH range. Additionally, the pH dependent leaching behavior is in-line with the observation of Figure 5.2a, where an increasing leaching for As and V with a higher activator molarity (higher pH) was observed. The results of the pH dependence test also show that the leaching of Mo and Se is independent of the pH in the alkaline region (also in line with observations from Figure 5.2).

The Cr leaching curve shows clear anionic behavior above pH 6, indicating that the dominant form leached towards higher pH is Cr(VI), which is consistent with observations in regular cementitious materials [16,23]. Still, these concentrations are relatively low compared to the bandwidth for regular blended cements (Figure 5.5e) and observed within the literature [19]. It is known that Cr(VI) is reduced to Cr(III) in blended Portland cement materials which contain PCFA in combination with a strong reducing agent such as GGBS. Additionally, in materials that only contain PCFA and no GGBS, Cr(VI) is not reduced and therefore shows an elevated concentration. To this end, it is considered that GGBS can be used as a tuning parameter to control the leaching of Cr from AAM. Still, from the observation that the dominant leached form from AAM is likely to be Cr(VI), it does not imply that all Cr in AAM is in this form. If it is assumed that all of the Cr(VI) is leached at pH 13 (~0.2 mg.kg), then the remaining majority of Cr in the sample (~50 mg.kg) can be assumed to be in the form of Cr(III) and is not leachable.

When effects of carbonation during the use in a next life phase is considered, the ageing effect will lower the pH from about 12-13 to an expected final pH of 8-9, resembling the pH of calcite in equilibrium with the atmosphere [22,26]. It is expected that the leaching of V, Cr and As from AAM will decrease towards the end pH of around 8-9 (e.g. compare the leaching at pH 12-13 to the leaching at pH 8-9). The leaching of Se and Mo is expected to remain similar when the granular AAM is subjected to carbonation processes during the next life phase in e.g. aggregate or road foundation. Typically, for regular Portland cementitious materials, the release trend upon carbonation for most oxyanions is the opposite to AAM, i.e., showing an increased leaching behavior upon carbonation and pH lowering as a result of the dissolution of ettringite and the formation of calcite [19,21,22,26–28].

Furthermore, the leachable concentrations of oxyanions from AAM can be significantly lowered by optimizing the GGBS content in the mixture as was shown in Figure 5.3. The results indicate that optimization of the GGBS content might result in a leaching performance of AAM that is generally in line with the results of the blended Portland cement range (Figure 5.5).



Figure 5.5: pH Dependent release of V (a), As (b), Se (c), Mo (d) and Cr (e) from 28 day old AAM mortar mixture B3 and of single PCFA and GGBS and from that of the Portland cement leaching test results from previous studies [19,32,33]. Data measured with the batch leaching test (L/S 10) in accordance with EN 14997. Green triangles: leaching of single PCFA. Red circles: Leaching of AAM mortar as granular material. Blue diamonds: leaching of single GGBS. Black diamond: own pH of the mortar sample. Dashed horizontal line: SQD leaching limit of element for granular building materials for open mortars with blended Portland cements (CEM III/B, CEM II/A-S, CEM II/A-S, CEM II/B-F and CEM V/A). The grey lines: 5% and 95% percentiles represent application [3]. The legend is common for Figures 5.5 and 5.6.



with blended Portland cements (CEM III/B, CEM II/B-S, CEM II/A-S, CEM II/B-F and CEM V/A). The grey lines: 5% and 95% percentiles represent that of the Portland cement leaching test results from previous studies [19,32,33]. Data measured with the batch leaching test (L/S 10) in accordance with EN Figure 5.6: PH Dependent release of Si (a), Al (b), Ca (c) and S (d) from 28 day old AAM mortar mixture B3 and of single PCFA and GGBS and from mortars 14997. Green triangles: leaching of single PCFA. Red circles: Leaching of AAM mortar as granular material. Blue diamonds: leaching of single GGBS. Black diamond: own pH of the mortar sample. The legend is common for Figures 5.5 and 5.6.

6 Conclusions

The main conclusions that can be drawn from this chapter are as follows:

- The oxyanion content and leaching, within a natural and or highly alkaline aqueous environment, is for PCFA much more significant for As, Se, V, Mo and Cr in comparison with GGBS, which mainly contains and releases V.
- Compressive strength progression of AAM is strongly influenced by the mortar mixture composition by varying: NaOH activator alkalinity, GGBS-PCFA mass proportion of the total binder and L/B ratio.
- Total element leaching of AAM concretes was far below the Dutch regulatory leaching limit values for monolithic materials; even though AAM strongly differed in mixture composition (NaOH activator alkalinity, GGBS-PCFA mass proportion of the total binder and L/B ratio).
- Granular state (aggregate) AAM show a significant difference in leaching strongly influenced by the mixture design. The release of As and V increases with a higher mixture L/B and with a higher activator molarity and the leaching of As, Mo, Se and V strongly increases as a direct function of a higher PCFA content within the GGBS-PCFA binder composition.
- Oxyanion leaching is strongly influenced and related to the binder composition. A higher PCFA content significantly increases and a higher GGBS significantly decreases the leaching of As, Se, V, Mo and Cr from granular state AAM. Aggregate meets the Dutch SQD leaching limits for open application of granular building materials when the PCFA content within the total binder composition is at maximum 30 wt.%.
- The leaching of AAM aggregate has been tested (pH dependent test) to identify and simulate pH lowering due to potential carbonation processes. Leaching of Mo, Se, and Cr are, more or less, insensitive to pH lowering (pH range 13 to 8), although V and As show a strong decreasing trend when the material pH lowers. Overall oxyanion behavior and concentrations fit relatively well within the 5% and 95% percentile leaching range of blended (slag and fly ash) Portland cements. However, the leaching of V and As from AAM aggregate is higher at high pH (> pH 11), than in blended Portland cementitious materials.
- The obtained understanding of the oxyanion leaching behavior is crucial to design new AAM (concrete) construction and/or building materials using secondary minerals that meet the regulatory leaching limits, both at the initial use (monolithic) and at the end of the service life after demolition (aggregate). This development stimulates mineral circulation in useful applications with acceptable leaching characteristics.

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CHAPTER 6

High performance of treated and washed MSWI bottom ash granulates as natural aggregate replacement within earth-moist concrete*

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Simplified model: solid waste to mineral circularity



Graphical abstract

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Abstract

Municipal solid waste incineration bottom ash was treated with specially designed dry and wet treatment processes, obtaining high quality bottom ash granulate fractions (BGF) suitable for up to 100% replacement of natural gravel in concrete. The wet treatment (using only water for separating and washing) significantly lowers the leaching of e.g. chloride and sulfate, heavy metals (antimony, molybdenum and copper) and dissolved organic carbon (DOC). Two potential bottom ash granulate fractions, both in compliance with the standard EN 12620 (aggregates for concrete), were added into earth-moist concrete mixtures. The fresh and hardened concrete physical performances (e.g. workability, strength and freeze-thaw) of high strength concrete mixtures were maintained or improved compared with the reference mixtures, even after replacing up to 100% of the initial natural gravel. Final element leaching of monolithic and crushed granular state BGF containing concretes, showed no differences with the gravel references. Leaching of all mixtures did not exceed the limit values set by the Dutch Soil Quality Decree. In addition, multiple-life-phase emission (pH static test) for the critical elements of input bottom ash, bottom ash granulate (BGF) and crushed BGF containing concrete were assessed. Simulation pH lowering or potential carbonation processes indicated that metal (antimony, barium, chrome and copper) and sulfate element leaching behavior are mainly pH dominated and controlled, although differ in mechanism and related mineral abundance.

Keywords: Heavy Metals, Characterization, MSWI Bottom Ash, Leaching, Strength Properties

1 Introduction

One of the sustainability strategies of the European Union (EU) is developing a circular economy. Potential waste and secondary materials are promoted to be re-used or recycled and subsequently applied within comparable or new processes and or applications. Hence, initial waste materials are regarded as potential new resources. This approach will ultimately lower the amount of necessary primary materials and potentially reduce the amount of materials that go into landfills. In relation to this strategy, the EU Construction Products Regulation (CPR 305/2011/EU) has come into force. This EU regulation attempts to obtain more knowledge and junction, creating a generic and level playing field between EU member states in regard to the re-use application of waste and or secondary materials (related to environmental quality) within processes.

The Netherlands is already facilitating the re-use of many types of secondary materials within construction works by a clear and workable regulation regarding the application of building materials [1]. In addition, specific actions are initiated by the government to stimulate re-use in a sustainable way. One example is the re-use of Municipal Solid Waste Incinerator (MSWI) bottom ash, were the Dutch industry has signed a 'green-deal' with the central government to improve (towards the year 2020) the physical and environmental quality of the treated ashes. Initiating a more environmental, economically efficient and sustainable bottom ash use in constructions e.g. open granular applications for road base layers and/or secondary aggregate in asphalt and cement concrete applications.

A general, conventionally dry treated MSWI bottom ash is mainly composed noncombustible materials e.g. slag, stone, glass, ceramic, sand and metallic metals. Where especially metal recovery is of high economical value regarding the extraction of valuable scarce resources e.g. copper, lead, messing, zinc, aluminum and iron [2]. The final mineral ash composition primarily consists of silicon, calcium, iron and aluminum containing structures e.g. quartz, calcite, hematite and ettringite [3–7]. The mineral compositions can vary time-to-time between the incinerators in relation to solid waste input and incineration conditions. Additionally, these conditions also effect the abundance and moderate concentrations of heavy metals and salts that are within the ashes [6,8].

Treated mineral bottom ashes are to some extent comparable to the most widely used raw concrete aggregates and are therefore possibly useful as mineral additions in various construction material applications [7,9-17]. As such, a well-designed bottom ash granulate could potentially play an important role in the sustainable progress within Portland cement mixtures, as an aggregate alternative for primary sand and gravel. Additionally, this relative new ash application could stimulate reuse of the relatively fast growing (millions of tons) bottom ash quantities produced world-wide and that are currently and mainly stored in landfill sites [18]. To the authors knowledge, only a few available recent studies deal with mechanically treated MSWI bottom ash fractions in concrete, where currently no significant and satisfying results have been obtained. Research does show that, overall improved ash-containing concrete performance is obtained with wet treated ashes in comparison with only dry treated [19–21]. Kuo et al. [22] and Yang et al. [23], attribute the difference to the finding that the liquid phase extracts and reduces a large part of the available and potentially disturbing salts, heavy metals and fine particles, present within the ashes. To summarize literature on bottom ash containing concretes compared with the Portland reference systems the following main drawbacks have been observed:

- Strong and substantial decline of fresh concrete workability [21,24].
- Severe matrix expansion and cracking by hydrogen gas production [24,25].
- Cement hydration retardation by abundant disturbing substances [26].
- Severe increase of matrix porosity and permeability due to gas bubble formation [19,24,25].
- Moderate to high loss of mechanical strength [19–21,24].

Despite these drawbacks, the mentioned studies also report multiple ash related upsides e.g., relatively good particle distribution for concrete application, equal to slightly lower material density compared to concrete aggregate [20], moderate to high ash particle abrasion properties, pozzolanic reaction of bottom ash particles [21] and very low economical material costs when applied as granulate.

Knowing both disadvantages and advantages, the authors elaborated a new and promising approach; applying a specially developed dry and wet treatment on the ash before being utilized in earth-moist (zero-slump) concrete mixtures. This treatment approach and related concrete design (which will be performed on large scale and real life production pilots) has never been considered. Until now, all published work focuses on laboratory-scale production by applying relatively wet (high consistency) concrete mixture designs (liquid/ binder ratios of ≥ 0.4 - 0.6) instead of dry (low to zero consistency) earth-moist designs. Interestingly, research on the earth-moist concrete production and related products are rarely published [27], due to difficulties to produce and simulate this production process at the laboratory scale. In practice, the production requires an extremely high pressure compaction in combination with an ideal particle packing and mixture consistency.

When applying the treated ash, the related earth-moist concrete material properties could trigger an optimized result and consequently ash usage can then be favored. Identifying the potential synergy of this approach: firstly, earth-moist concrete has no slump or measurable workability and consistency is mainly determined by the compaction rate (green strength) in combination with visual inspection. Hence, workability loss initiated by the ash at its higher water demand is not of influence on the fresh concrete performance. Secondly, the relatively high porosity of earth-moist concrete is able it to capture potential hydrogen gas production from the bottom ash, preventing matrix expansion and related crack formation. Thirdly, the dry and wet ash treatment reduces the amount of disturbing substances within the bottom ash, therefore accordingly the potential negative interferences on the cement hydration can be minimized or neglected. Therefore, the following most important parameters (substances) in bottom ash treatment which influence the concrete performances that need to be controlled to obtain valuable bottom ash granulate fractions (BGF) are:

- Recovery of as much of the non-ferrous (aluminum and zinc) and ferrous metallic metals as possible that cause potential concrete expansion, cracking and pop-out problems due to hydrogen formation [13,19].
- Extraction of the majority of fine and coarse unburned organic particles and their released organic structures that potentially disturb cement hydration processes [26].
- Reduce the total percentage of very-fine, mainly organic micrometer particles. These particles could interfere with the needed particle packing approach, increase water demand in the mixture, lower fresh concrete workability and retard cement hydration.
- Optimize bottom ash particle-size distribution to obtain an appropriate mineral granulate replacement for natural gravel.
- Reduce the amount of potential leachable salts, heavy metal and organic structures that influence the cement hydration or can leach into soil and groundwater systems [28–32].

Given these characteristics, this chapter focusses on treatment optimization of raw bottom ash where 1) all of its initial disturbing substances are selectively removed and 2) the (BGF) material is tuned to an ideal particle-size distribution. Furthermore, bottom ash granulates are first produced in a pilot experiment which combines specially designed dry and wet treatment processes. In a second pilot production, pre-fabricated earth-moist concrete elements are produced by replacing various mass percentages (0-100 %) of the natural gravel by the BGF.

The overall aims of the chapter are:

- Investigate the suitability of the designed bottom ash treatment processes.
- Characterize the initial BGF material properties and their performance within open granular and concrete application.
- Place emphasis on the leaching emissions and mechanisms in the first, second and multiple-use phases of the concrete products containing BGF as gravel replacement.

The novelty of this work is primarily the comprehensive approach to develop earthmoist concrete containing treated bottom ash. Different physical/chemical parameters important for concrete development are combined to obtain a novel bottom ash treatment process for substituting sand/gravel in concrete.

2 Treatment process for MSWI bottom ash

Physical and chemical characterization of fresh MSWI bottom ash is of great importance, in producing qualitative useful concrete granulates [4,13,19]. Therefore, raw, untreated ash requires upgrading treatments due to its relatively heterogenic and chemically instable properties. One method, for example, is extracting all the nonmineral disturbances e.g. unburned and metallic materials. In this study, a sequence of treatment steps is performed to obtain useful granulates. Within this pilot production, up to one thousand tons of granulate was produced from MSWI bottom ash from a Dutch municipal solid waste incinerator located in Duiven. The ash was treated stepwise with dry and wet separation processes (explained below in the steps 1-4), producing optimal bottom ash granulate fractions (BGF) which were further characterized and tested as granulate in earth moist concrete. The performed BGF production process is a combination of current common practice [33-35] and new developed dry and wet mechanical separation techniques composed of four separate treatment steps (described below). An overview of the processes and the different bottom ash fractions is shown in Figure 6.1. Note that the total material input or the bottom ash mineral fraction (BMF) of 43 % within the wet-treatment process increased to a 49 % output. This effect is caused by water washing and saturation of the relatively porous BGF and the generated sludge fraction, which has a 50 % water content.



Figure 6.1: Mass balance of bottom ash granulate production and treatment process.

Step 1. Weathering of fresh MSWI bottom ash

Freshly produced and quenched MSWI bottom ash (BMF) was stored outside and naturally weathered for \geq 3 months. During this period, the ash slowly dries and neutralizes towards a more physically and chemically stable material [31,36,37]. This step further enhances the decrease of leaching potential of inorganic elements such as heavy metals [29,38–40]. Additionally, during this time period and related high pH \geq 11, significant oxidation of metallic ferrous and non-ferrous metals occurs.

Step 2. Dry separation MSWI bottom ash and metal recovery

Weathered bottom ash was first mechanically crushed and particles (< 400 mm) of mainly 'unburned' and metallic materials were extracted using a screener and powerful overhead magnet. The generated bottom ash mineral fraction (BMF) was further dry separated, in the same screener, into two fractions, BMF 0-12mm and 12-31.5 mm. Fraction 0-12 mm was additionally separated into two fractions, BMF 0-2/3 mm (which was not further treated) and BMF 2-12 mm. Both fractions 2-12 mm and 12-31.5 mm were further processed using magnets, eddy current systems and fluff extraction apparatus to extract the maximum amount of unburned and metallic materials e.g. ferrous, non-ferrous and stainless steel [2]. Finally, both fractions were mixed together resulting a in a BMF 2/3-31.5 mm bottom ash fraction.

Step 3. Wet separation and washing treatment

The BMF 2/3-31.5 mm was the input for the wet separation process. For this treatment, a specially designed mobile water separating-cleaning plant was built. It is a water consuming process with a liquid to solid ratio (L/S) of approximately 1:2 (contact-time ± 10 min.). By washing and scrubbing potential initial material disturbances e.g. very fine particles and mobile organic and inorganic leachable contaminants (organic acids, heavy metals and salts) were removed. This method was applied earlier by several other authors [20,23,41,42]. The pollutants were mainly concentrated in the sludge fraction, resulting in a coarser residue with an overall better environmental quality. Figure 6.1 shows that five different fractions were produced: sludge < 80 µm, three fractions of BGF 0-4 mm, 2-8 mm, and 8-16 mm, and an oversize BMF > 31.5 mm.

Step 4. Final granulate treatment for concrete application

Finally, both coarse fractions (BGF 2-8 mm and 8-16 mm) were additionally treated before being used in Portland cement (alkali based) concretes. Due to washing, the bottom ash was further crushed or broken to release and additional fraction of metallic non-ferrous and ferrous particles that were initially covered by ash agglomerates. These metals needed to be extracted from the material to obtain a higher metal recovery and reduce their potentially damaging effect on the concrete. Metallic metals (e.g. Al and Zn) potentially initiate hydrogen gas production that can subsequently lead to expansion problems with fresh and hardened concrete and interfere with the cement hydration reaction [25]. Therefore, both BGF fractions were treated with magnetic separator systems to further reduce the metallic metal contents.

3 Materials

The pavement stones (concrete mixtures) were produced with a blended Portland slag cement, a CEM III and the curbstones with a blended CEM II; both in combination with a very small addition of polycarboxylate superplasticizer (SP). Furthermore, groundwater, natural river sand 0-4 mm, and rounded gravel fractions of 2-8 mm and 8-16 mm were used. Within the mixture design, natural aggregate replacement was done by addition of the two bottom ash granulate fraction (BGF), a 2-8 mm and 8-16 mm, picture of fraction is shown in Figure 6.2.



Figure 6.2: Bottom ash granulate fraction 8-16 mm.

4 Concrete mixture design and production

Concrete mixtures with the addition of two types of BGF 2-8 mm and 8-16 mm were tested. Replacement levels of both the original natural gravel types for BGF were 0 %, 40 %, 70 % and 100 % by mass of volume. All mixtures are described in Tables 6.1a and the related aggregate replacement levels is described in Table 6.1b.

Mixture	CEM	Sand 0-4	Gravel 2-8	Gravel 8-16	BGF 2-8	BGF 8-16	Water	SP	Cal. density	W/C ratio
PS-0%	288	1010	971		0		104	0.52	2374	0.36
PS-40%	288	1010	568		360		104	0.52	2331	0.36
PS-70%	288	1010	274		630		104	0.52	2307	0.36
PS-100%	288	991	0		901		104	0.52	2283	0.36
CS-0%	309	975	634	324		0	111	0.43	2354	0.36
CS-40%	309	994	385	171		360	111	0.43	2331	0.36
CS-70%	309	994	212	57		631	111	0.43	2314	0.36
CS-100%	309	955	19	0		901	111	0.43	2295	0.36

Table 6.1a: Mixture design (composition by mass of volume) of earth-most concrete pavement- and curb stones.

All values in kg/m³.

Table 6.1b: The aggregate replacement level (volume) of earth-most concrete pavement- and curb stones described in Table 6.1a.

Mixture	Sand 0-4	Gravel 2-8	Gravel 8-16	BGF 2-8	BGF 8-16
PS-0%	51%	49%		0%	
PS-40%	51%	29%		20%	
PS-70%	51%	14%		35%	
PS-100%	50%	0%		50%	
CS-0%	50%	33%	17%		0%
CS-40%	51%	20%	9%		20%
CS-70%	51%	11%	3%		35%
CS-100%	49%	1%	0%		50%

Two element products were produced and tested; curbstones (CS) with dimensions of $1000 \times 200 \times 100 \text{ mm}^3$ (length × height × width) and pavement stones (PS) with dimensions of $210 \times 80 \times 70 \text{ mm}^3$, shown in Figure 6.3.





Figure 6.3: Curb stone with BGF 8-16 mm (a) and pavement stone with BGF 2-8 mm (b).

Both elements were constructed out of two layers of concrete, a specific high performance top layer which constitutes around 10 % and a bottom layer which constitutes around 90 % of the total construction. BGF was added as gravel replacement in the bottom layer concrete, within the top layer BGF is at the moment not applicable as this is not in compliance to the current Dutch standards. Within the analyses, strength tests were performed on the total layer construction and all other tests were specifically performed on the BGF containing bottom layer. The numbers behind the material abbreviations (0-100 %) in Table 6.1, addresses the total amount of natural granulate replacement by BGF, within the tested concrete mixtures. Within the reference mixture 0% of BGF was used.

Factory scale production was chosen over laboratory experiments to overcome scaling problems (difficult to obtain representative products at lab-scale), and was performed at the site of 'de Hamer' in the Netherlands. Mixing was done by a wheeler batch mixer, around 1m³ per batch, with total batch times of 3 min. Fresh concrete was compacted within 10 min. after production. After production, the specimens were kept in a climate chamber for approximately 24 h. at 25-30 °C with a relative humidity > 60 %. From the climate chamber, elements were stored outside and sealed with a plastic sheet, to reduce unwanted water evaporation. In total, several hundred pavement stones and up to one hundred curbstones were produced.

5 Experimental methods

5.1 Physical material testing

The material properties of the used natural sand and gravels and produced BGF fractions were analyzed in accordance with NEN-EN 12620 (2002+A1:2008 NL). Additionally, BGF fractions were tested in accordance with the Dutch product standard BRL 2507 [43] which was specifically developed as a supplement guideline for use of bottom ash fractions within Portland cement and or blended cement concrete mixtures. The final concrete performance was measured for multiple material parameters, in accordance with their product standards. For strength measurements, in accordance with the standard, specimens were first water soaked for 24 h. Total water saturation

reduces possible internal stresses which could lead to unwanted deviations. Strengths were measured in accordance with the standard at 7 and 35 days. Flexural strength for curbstones (3 measurements per data point) was measured in accordance with the BRL 2314 (2005, class 2, mark T). Tensile strength for pavement stones (8 measurements per data point) were measured in accordance with BRL 2312 (2005). In addition, pavement stones were tested on freeze/thaw deicing salt resistance (3 measurements per data point) in accordance with NEN-EN 1338:2003 (E) annex D. As a preparation for the freeze/thaw measurements, stones were vertically cut in the middle (obtaining a smooth and representative surface) to test only and specifically the bottom BGF containing surface layer. All tested concrete specimens were randomly taken from the production.

5.2 Chemical material testing

For the leaching analysis all granular and monolithic samples were taken from both the granulate and concrete materials. Granular samples were crushed to < 4 mm before testing, in accordance with the appropriate test method. In the case of hardened concrete, \emptyset 100 mm cylinders were drilled and crushed before granular material was tested. All monolithic samples were drilled out of the concrete elements, sample size: cylindrical \emptyset 100 mm with 100 mm in height. The testing of granular materials was performed with the compliance percolation test in accordance with NEN 7383 (2004 NL). In this test, the leaching is measured as a function of the L/S ratio by percolation of the bottom ash. The cumulative emission at L/S= 10 L/kg is measured in one cumulative eluate fraction. Monolithic materials were tested using the tank leaching test in accordance with NEN 7375 (2004 NL). All tested concrete 'monolithic and granular samples' were around 35 days old when the tests were performed. Chemical analysis of leachates from leaching tests was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Chloride (Cl), bromide (Br) and sulfate (SO₄) were analyzed using ion chromatography (IC). Fluoride was analyzed by flow injection analyses with spectroscopic detection.

Batch pH-static leaching experiments were carried out according to EN 14997 on subsamples that were each equilibrated for 48 h. at a predetermined pH value between pH 2 and 12. The samples BMF 0-31.5 mm, BGF 2-16 mm (mixture of BGF 2-8 mm and 8-16 mm) and concrete sample PS-100 % were used for the pH dependence leaching test. Within this method 15 g of dry bottom ash was suspended in 150g nanopure demineralized water (L/S ratio of 10 L/kg) in acid-cleaned 300 mL PTFE vessels, under continuous stirring at 20 °C in contact with the atmosphere. The pH of the different suspensions was controlled using solutions of 1M HNO₃ and NaOH (analytical grade) and a computerized pH-stat system. After the equilibration period, the suspensions were filtered through 0.45 μ m membrane filters. The eluates were acidified with concentrated HNO₃ (Suprapur[®]) and analyzed by ICP-AES to obtain solution concentrations of a wide spectrum of major and minor elements. It was assumed that total Sulfur (S) as measured by ICP-AES equated to SO₄ (factor 3 to convert S to SO₄).

6 Results and Discussions

In this section, two possible granular application routes for the produced BGF fractions are investigated. First, produced BGF was tested for potential application as a granular construction product for open application in road bases or embankments. Second, BGF was tested as natural gravel replacement within earth-moist concrete.

6.1 Bottom ash treatment and application feasibility as a granular construction material

The produced raw, untreated bottom ash (BMF) was subjected to several dry and wet separation steps to upgrade the environmental quality and to produce fractions with desirable physical properties, see Section 2.1. To assess the open application re-use possibilities, the bottom ash input material, which was combined with several fractions at different steps in the process and the final granulates, leaching was tested using the percolation leaching test (NEN 7383). The results in Table 6.3 show a number of interesting features regarding the treatment processes.

The input material (BMF 0-31.5 mm) already had a relatively low pH in comparison with freshly produced bottom ash. This is most likely a result of the natural weathering period of 3 months. Its pH decrease as a result of weathering has been reported by other authors [28,44,45]. The leaching of most regulated substances did already comply with the limit values [1] for an open application. However, the leaching of antimony (Sb), copper (Cu), chloride (Cl) and sulfate (SO₄) exceeded their limit values (bromide (Br) is just below the limit value). It is known that the leaching of these elements can be close to the limit values for open application [44], emphasizing the need for quality improvement of dry treated bottom ash. The further dry separation into a fine fraction (BMF 0-2/3 mm) and a coarse fraction (BMF 2/3-31.5 mm) clearly indicates that the relatively mobile substances Mo, Sb, Br, Cl and SO_4 are preferentially concentrated in the fine fraction. It is postulated that these elements are already dissolved mostly in the pore water of the bottom ash and are transferred to the fine fraction together with most of the water from the bottom ash. Furthermore, in the case of sulfate, release is mainly controlled by gypsum solubility [28,32]. Gypsum, a sulfate source, is believed to be vulnerable to the sieving treatments due to its low mineral brittleness. It is easily crushed during sieving and becomes more concentrated in the fine BMF 0-2/3 mm fraction. As a result, the coarse BMF 2-31.5 mm shows a substantial reduction of sulfate and chloride and, to a somewhat lesser extent, bromide leaching. It is noted that the Mo leaching in the coarse fraction seems to be somewhat higher than the original input material. Which might be explained by the weak pH dependent adsorption of Mo by reactive iron/aluminum (Fe/Al)-(hydr)-oxide surfaces of less reactive courser-sized bottom ash particles e.g. glasses and ceramics [29,32]. The same mechanism might also explain the leaching of Sb between the fractions. Overall, the results of the dry separation treatment show that this technology positively affects the leaching of Mo, Sb, chloride and sulfate

and to a lesser extent bromide. However, the produced coarse fraction (BMF 2-31.5 mm) does not comply with the criteria of open application (SQD) with respect to the leaching of Cu, Cl and SO₄. The leaching of Sb and Mo are close to their limit values.

Material	BMF	BMF	BMF	BGF	BGF	BGF	Limit
	0-31.5	0-2/3	2-31.5	0-4	2-8	8-16	Granular material
n	3	2	1	1	1	1	
pН	8.41	8.14	9,04	8.46	8.41	8.45	no limit
EC	1681	2495	730	956	696	654	no limit
Sb	0.55	0.68	0.25	0.30	0.30	0.28	0.32
As	0.08	< 0.10	0.05	< 0.10	< 0.10	< 0.10	0.90
Ba	0.39	0.39	0.50	0.28	0.20	0.17	22.00
Cd	< 0.0085	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.04
Cr	0.05	< 0.10	0.05	< 0.10	< 0.10	< 0.10	0.63
Со	0.04	< 0.10	0.03	< 0.10	< 0.10	< 0.10	0.54
Cu	1.53	1.45	1.30	< 0.15	< 0.15	< 0.15	0.90
Hg	< 0.0012	0.005	0.00	< 0.005	< 0.005	< 0.005	0.02
Pb	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	2.30
Мо	0.51	1.20	0.84	0.32	0.23	0.20	1.00
Ni	0.09	< 0.10	0.05	< 0.10	< 0.10	< 0.10	0.44
Se	0.01	< 0.039	0.01	< 0.039	< 0.039	< 0.039	0.15
Sn	0.02	< 0.10	0.02	< 0.10	< 0.10	< 0.10	0.40
V	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	1.80
Zn	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	4.50
F	5.6	2.3	2.4	4.0	2.6	2.4	55
Cl	2725	4950	1700	550	570	687	616
SO ₄	6533	11000	3200	3367	1833	1393	2.430
Br	18.8	25.0	14.0	2.8	3.0	3.5	20

Table 6.3: Total element emission measured with the percolation test (NEN 7383) of granular state bottom ash fractions from different treatment processes.

All values in mg.kg dm.

n: Sample amount.

The bottom ash was also wet treated with a water separation step to a cumulative L/S ratio 1-2 L/kg. The use of water in this step also implies that bottom ash is washed during separation, to reduce its mobile constituents [23]. The leaching of the three resulting bottom ash granulate fractions (BGF) were analyzed with the percolation test (Table 6.3). In general, this treatment step had a very positive effect on the reduction of

leaching of the mobile elements Sb, Cu, Mo, Br, Cl, and SO₄. The dry and wet separation of bottom ash shows potential, reducing the leaching of BGF that than can comply with the SQD leaching criteria for open application; although Cl and SO₄ leaching can sometimes still be critical. However, it is observed that the Cl content is strongly reduced within the BGF and a slight Cl increase in the washed BGF as a function of larger particle size is observed, shown in Table 6.3. This effect might be explained by the higher porosity of larger particles that can lead to higher (chloride containing) water absorption and, hence, more dissolved Cl in that bottom ash fraction. If necessary, a further reduction of leachable Cl and SO₄ from the BGF fractions can be obtained by increasing the L/S ratio and contact time during washing and/or the water refreshing rate within the process [23,46]. An important observation is that during the wet treatment process the Sb leaching is not lowered when comparing input BMF 2-31.5mm with both washed course BGF fractions. However, this effect is noticeable when comparing BMF 0-2/3 mm input with the washed 0-4mm BGF fraction where Sb emission is reduced > 50 %. In addition, in a preliminary pilot washing test a lowering effect on Sb release was also noticed, where the input bottom ash fraction 0-31.5 mm contained about 1.0 mg.kg dm and the produced granulate fractions 4-20 mm about 0.25-0.44 mg.kg dm (reduction of about > 50 %). This effect could be attributed to availability and the washing out of a large part of the soluble state penta antimonite (Sb_2O_5) , which is likely to be present in weathered bottom ash eluate [28,44,47,48]. Due to washing this metal species is transferred to the washing water and the produced sludge residue. However, the Sb release from the granular material can still be at critical limit value for open application. Considering the leaching of all regulated substances in the BMF and BGF samples (Table 6.3), it is concluded that the wet separation technology strongly improves the overall environmental quality of most of the initial mobile abundant elements (Sb, Ba, Cu, Mo, Cl, SO₄ and Br). Although in the case of the course washed fractions, Sb reducing is less noticeable.

Finally, the results of this study show that both dry and wet separation are favored in order to improve the initial environmental quality of the washed course-size bottom ash fractions. The leaching of Cl and Sb could remain critical to meet the SQD limit values for an open application (using an L/S ratio of 1 to 2). Therefore, the option to use the BGF as a gravel replacement in concrete was also assessed.

6.2 BGF application as a gravel replacement in concrete

Previous research showed that particles shape, distribution, material porosity and density of MSWI bottom ash aggregates differs compared with natural aggregates which, in the end could influence the final fresh and hardened physical properties of a cement based concrete product [4,5]. To gain optimal and effective replacement properties, the particle-size distribution (PSD) of both BGF fractions (Figure 6.4) were modified by adjusting the sieving mesh size within the wet treatment to resemble natural aggregates.



Figure 6.4: Particle-size distribution of natural gravel and BGF fractions of both at 2-8 mm and at 8-16 mm size fractions.

When comparing their PSD, the recycled and natural materials do show some difference in the particle shape and to a lesser extent also in particle-size distribution, although the variation within the PSD of the BGF fractions are limited to about 5-15%. The variation fits within the criteria of the NEN-EN 12620 (aggregates for concrete). This also shows that with the wet treatment process is effective with which an adjustable BGF particle distribution can be obtained. Furthermore, the BGF is more rectangular shaped than the natural round aggregate which mainly originates from the slag, glass and ceramic particles. BGF shows a higher material porosity and related water absorption, mainly caused by the porous slag particles.

The analyzed material properties of the BGF relevant for the requirements to produce concrete are described in Table 6.2. Parameters such as Loss on ignition (LOI 500), Alkali equivalent, Metallic Al (+Zn) and the sulfur trioxide (SO_3) content are not measured for natural gravel as these are only relevant for bottom ash fractions that are considered for use in concrete. The requirements for re-use of bottom ash in concrete and the test methods to be used are described in Dutch guidance document [43].

Parameter	BGF 2-8	BGF 8-16	Sand 0-4	Gravel 2-8	Gravel 8-16	CEM II	CEM III	Limit ¹
LOI 500 (% mass)	0.95	0.59	n.m.	n.m.	n.m.	n.m.	1.0	≤ 5.0
Alkali equivalent (% mass)	0.14	0.16	n.m.	n.m.	n.m.	0.59	0.77	≤ 0.2
Metallic Al (% mass)	0.47	0.29	n.m.	n.m.	n.m.	n.m.	n.m.	
Metallic Al+Zn (% mass)	0.73	0.80	n.m.	n.m.	n.m.	n.m.	n.m.	≤ 1.0
SO ₃ (% mass)	0.15	<0.03	n.m.	n.m.	n.m.	n.m.	n.m.	≤ 0.8
Anhydrite (% mass)	n.m.	n.m.	n.m.	n.m.	n.m.	2.8	3.3	
Chloride content (% mass)	≤ 0.03	≤ 0.03	≤ 0.003	≤ 0.003	≤ 0.003	0.04	0.06	
Los Angeles (LA) coefficient	33	31	> 35	> 35	> 35	n.m.	n.m.	
Density $P_{\rm rd}$ (kg/m ³)	2400*	2250*	2640	2570	2570	3000	3020	≥ 2000
Water absorption 24h (% mass)	6.9	6.8	0.2	1.3	1.3	n.m.	n.m.	
n.m.: not measured.								

Table 6.2: Properties of raw materials for concrete production.

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]: Limit values in accordance to NEN-EN 12620/ NEN 5905. *: $\pm 100~{\rm kg/m^3}.$

Table 6.2, indicates that all tested BGF parameters meet their limits specified in NEN-EN 12620 and NEN 5905. Therefore, it is concluded that the BGF properties seem to be compatible with the requirements to replace natural gravel with BGF in concrete. Another important parameter that determines the application of BGF as aggregate replacement in concrete is the emission of contaminants from the concrete to soil and ground water. Hence, the tank leaching test was performed on concrete curb stones (CS) samples to assess leaching using gravel replacement rates from 0-100%. The results reported in Table 6.4 show that all BGF containing concrete mixtures comply with the limit values for monolithic construction materials. However, with an increasing replacement rate of BGF, it results in even slightly lower emissions of metals, although it is unclear whether this difference is significant. A possible explanation for this effect, is sorption and or complexation of leachable mobile 'heavy' metals on reactive Fe/Al-(hydr)-oxide and glassy surfaces within the porous slag. This would enable an additional barrier for further transport through the cementitious matrix [32,37,40,49]. Finally, only the leaching of Cl seems to be slightly increased within the sample with 100 % gravel replacement with BGF (CS-100). However, the measured Cl release (470 mg/ m^2) is still more than two orders of magnitude below the limit value (110.000 mg/m²). Overall, the results of the curb stones with BGF replacement rates between 0 % and 100 % have obtained an environmental quality which fulfills the requirements specified by the SQD.

6.3 Fresh and hardened concrete properties with increasing BGF content

During the production a total quantity of > 20 ton, earth-moist (zero slump) concrete was produced. The fresh material properties did not vary significantly as a result of the BGF (0-100 %) replacement. The consistencies and compaction rates of the mixtures, also known as 'green' strength, were all approximately equal (visually and manually judged). The additional mixture workability, also known as the open time or setting time, was likewise not influenced by increasing BGF quantities, although it is known that an increase of salts such as chloride and sulfate can accelerate or retard cement hydration [50]. The BGF fractions have up to 5 times higher water absorption rates (\pm 7 %) compared to natural gravel (\pm 1.3 %). This high absorption is mainly related to the porous slag content and could affect the workability properties when it is not fully saturated during usage. However, this high BGF water content may also act as an 'internal aquifer', which may further enhance internal cement hydration, resulting in a higher strength developed and matrix densification. This can be advantageous in earthmoist concrete mixtures, where a relative low water to binder (W/B) ratio is usually used, which would result in less efficient cement hydration by too low water contents.

Parameter	CS-0%	CS-40%	CS-100%	Limit monolithic material
pH start	11.6	11.6	9.8	no limit
pH end	11.9	11.9	11.5	no limit
Sb	0.4	0.4	0.4	8.7
As	4.0	4.0	2.2	260
Ba	19.0	20.0	3.3	1.500
Cd	0.1	0.1	0.04	3.8
Cr	4.0	4.0	2.2	120
Со	2.4	2.4	1.3	60
Cu	4.0	4.0	2.2	98
Hg	0.02	0.02	0.02	1.4
Pb	8.0	8.0	4.4	400
Mo	0.8	0.8	0.6	144
Ni	4.0	4.0	2.2	81
Se	0.6	0.6	0.3	4.8
Sn	1.6	1.6	0.9	50
V	8.0	8.0	4.8	320
Zn	16.0	16.0	8.7	800
F	128	96	49	2.500
Cl	88	80	470	110.000
SO	960	960	1200	165.000
Br	2	2	5	670

Table 6.4: Total element emission measured with the diffusion test (NEN 7375) of monolithic state curb stone concrete with increasing natural gravel replacement with BGF 8-16mm.

Al values in mg/m².

6.4 Concrete strength of pavement stones with BGF 2-8mm content

The pavement stones were constructed out of two concrete layers, a thin top layer (0.5-1.0 cm) and thick (7.0-7.5 cm) bottom layer. Only the bottom layer comprises of various replacement levels of BGF 2-8 mm. The whole stone specimen was tested on tensile strength development, from 0 % up to 100 % gravel replacement, of which the data is shown in Figure 6.5.



Replacement level gravel with BGF 2-8 mm (v/v %)

Figure 6.5: Tensile strength of pavement stones with increasing replacement levels (0-100 %) of BGF 2-8 mm for natural gravel 2-8 mm. Strength limit value at 35 days is 3.5 MPa.

The 7 days strengths were stable at around 3.7 MPa. At 35 days, strength results slightly increase at higher BGF replacement levels (from 4.5 MPa with 0 % BGF up to 5.1 MPa with 100 % BGF). However, this increase of 12% is deemed not to be significant with respect to the standard deviations of the analyses. Finally, all mixtures comply with the strength limit of 3.5 MPa at 35 days related to the standard. The authors propose several mechanisms to explain the observed increase in strength:

- The improvement of the attachment of inner particles due to the introduction of rougher and more rectangular shaped BGF. This enables a better mineral resilience between the aggregates and the cement binder in comparison with the round and more smoothly shaped gravel.
- The production of earth-moist concrete and its related low L/B ratio, is known as insufficient in generating an effective cement hydration. The mineral BGF matrix with its relatively high porosity and related high water absorption (\pm 7 %) could act as an inner aquifer which slowly releases water over time, resulting in more effective cement hydration and related strength growth.
- The smaller sized BGF contains a relatively high percentage of potential pozzolanic reacting bottom ash slag compared with the larger BGF fraction. This may act as reactive hydraulic aggregate to gain additional matrix densification and reduced porosity [21], resulting in higher strength development at 35 days and beyond [40,49]

To obtain a better understanding of the mechanisms behind these results, further research into the binding mechanism between the cement and the GBF in comparison with the gravel is necessary.

6.5 Concrete strength of curb stones with BGF 8-16mm content

The curb stone elements were similar to the pavement stones, produced out of two layers of concrete and BGF 8-16 mm was added only in the bottom layer. Their observed overall flexural strength development is somewhat different compared to the tensile strength of the pavement stones. At 7 days, a stable flexural strength (6.0 MPa) is gained at 0-40 % of BGF contents. However, strengths slightly decreased to 5.2 MPa at 70-100 % of BGF contents, of which the data is shown in Figure 6.6.





Figure 6.6: Flexural strength of curb stones with increasing replacement levels (0-100 %) of BGF 8-16 mm for natural gravel 8-16 mm. Strength limit value at 35 days is 5 MPa.

This overall effect is also reproduced at the 35 days strength development. At 0-40 % BGF addition, the 35 days strength reached an average of 6.6 MPa and decreased to an average of 5.8 MPa at higher than 40 % BGF contents. This 5.8 MPa strength means about 12 % loss compared to the reference, although it is not significant to the level of BGF added. In summary, a stable and one time strength loss at both 7 and 35 days was observed when more than 40 % of BGF was added. However, all curb stone mixtures comply with the 35 days strengths limit of 5.0 MPa, in accordance with the standard. The authors propose the following mechanisms for the observed strength decrease:

- Strength is influenced by the decline of particle's hardness/ abrasion (also known as Los Angeles coefficient). The hardness of the BGF 8-16 mm (value ≥ 31) is slightly lower compared to the BGF 2-8 mm (≥ 33) and both moderately lower compared to the natural aggregates (value ≥35), which results in a potential weaker matrix.
- The smoothness of particles can be of influence, as the BGF 8-16mm contains a relatively high content of large sized ceramics and glass particles compared to the BGF 2-8 mm. The poor shape of these coarse glass and ceramic aggregates causes a decrease in adhesive strength between the BGF aggregate and the cement paste, resulting in a

decreased flexural strength [51]. Overall, when using only the BGF 2-8mm instead of 8-16 mm fractions, as with the pavement stones, the observed strength loss may be further minimized.

• The course BGF, which has a lower specific surface area, contains much less potential pozzolanic slag particles compared with the fine BGF, which results in suppressed later age (35 days) strength development.

In consistency with the results of pavement stone strengths, further research on the aggregate/ cement binding mechanism is necessary.

6.6 Freeze-thaw deicing salt resistance of BGF containing pavement stones

An average Northern European climate requires specific freeze-thaw deicing salt resistance properties of outdoor concrete elements. In this study, these measurements were performed by determining the surface mass loss/m² of the bottom layers of pavement stones that contain the BGF 2-8 mm. The top layers of the pavement stones were not tested, as they are composed of only primary aggregates in combination with a higher binder content. As shown in Figure 6.7, the obtained mass loss results of the BGF containing concrete showed no significant increase with higher BGF contents. An average of ± 0.220 kg/m² is obtained with no significant differences between the 0% reference and 100% BGF replacement. All measured values are well below the prescribed limit of 1.0 kg/m². To summarize, even at higher BGF contents, and therefore higher porosity and potentially higher liquid adsorption, no performance loss was observed. This indicates that the performance of BGF related to freeze-thaw resistance is also in compliance, similarly to the natural gravels that are nowadays used as high performance top layer aggregates.



Replacement of gravel 2-8 mm with BGF 2-8 mm (v/v %) in pavement stones

Figure 6.7: Freeze-thaw deicing salt resistance of pavement stones with increasing replacement levels (0-100 %) of BGF 2-8 mm for natural gravel 2-8 mm. Limit value is 1 kg/m².

6.7 Potential emissions of bottom ash and concrete products in multiple life phases

6.7.1 Second life emissions of crushed and demolished pavement stones

Although the CPR indicates that emissions of construction products should not have an exceedingly high impact over the entire life cycle, there is currently no regulatory framework to assess this property. Therefore, additional experiments were performed indicating potential trends in material behavior in a second or multiple life phase. As a first step, it can be imagined that the BGF containing concrete ends as crushed construction and demolition product. This material can be used as recycled aggregate (second life) suitable as concrete aggregate, road base material or other granular construction applications and should be tested with a percolation leaching test according to Dutch regulations. Leaching data shown in Table 6.5, is obtained from crushed concrete with 0 %, 40 % and 100 % of BGF, replacing the gravel content. The results shows that the overall leaching of all crushed pavement stones is in compliance with the limit values for an open (granular) application used within a second life. Nevertheless, there seems to be a slight increase of only salts release at higher BGF replacement levels e.g. Cl, SO_4 and Br leaching. However these emissions remained far below the limit values.

Parameter	PS-0%	PS-40%	PS-100%	Limit granular material
pH end	12.4	12.2	12.1	no limit
Sb	0.01	0.01	0.02	0.32
As	< 0.05	< 0.05	< 0.05	0.90
Ba	5.00	4.40	5.00	22.00
Cd	< 0.001	< 0.001	< 0.001	0.04
Cr	< 0.05	< 0.05	< 0.05	0.63
Со	< 0.03	< 0.03	< 0.03	0.54
Cu	< 0.05	0.10	0.20	0.90
Hg	< 0.0004	< 0.0004	< 0.0004	0.02
Pb	< 0.10	0.26	< 0.10	2.30
Mo	0.07	0.07	0.11	1.00
Ni	< 0.05	< 0.05	< 0.05	0.44
Se	< 0.007	< 0.007	< 0.007	0.15
Sn	< 0.02	< 0.02	< 0.02	0.40
V	< 0.10	< 0.10	< 0.10	1.80
Zn	<0.20	<0.20	<0.20	4.50
F	1.2	1.2	1.4	55
Cl	60	89	160	616
SO ₄	38	54	66	2.430
Br	1.0	1.1	1.6	20

Table 6.5: Total element emission of granular state pavement stone concrete with increasing natura
gravel replacement with BGF 2-8 mm.

All values in mg.kg dm.

6.7.2 Multiple life emissions of crushed and demolished pavement stones

It is known that alkaline materials have a tendency to carbonate, take up CO_2 from the atmosphere during their life time [28,44,52]. The extent to which this process occurs and how it affects the material properties, is dependent on the material performance, application scenario and time. The potential endpoint of the Portland cement based carbonation process is the equilibrium with the mineral calcite (CaCO₃), resulting in a pH of about 8.5.

To approximate and compare potential effects of pH neutralization of the concrete pavement stones and to study this behavior, various bottom ash materials from this study were tested with the pH dependent leaching test e.g. untreated bottom ash (BMF 0-31.5 mm), treated bottom ash granulate (BGF 2-16 mm) and crushed pavement stone concrete (PS-100 %). The test results indicate trends in the emission of substances considering pH changes over the multiple life cycles of the material. This approach has also been used several times to identify release controlling phases and can assist in the development of treatment technologies to improve the leaching behavior [29,31,47,53,54]. The results of the pH dependence tests for Ba, Cu, Sb, SO₄ and chromium (Cr) are presented in Figure 6.8.





The leaching of barium from the pavement stones, in the relevant pH domain (pH 8-12), is substantially higher than both bottom ash materials (untreated BMF and the treated BGF materials in Table 6.3). These observations are also consistent with the percolation test results in Table 6.5, showing already a high Ba release from the reference concrete with 100 % gravel (PS-0 %). This observation might be explained by a lower amount of carbonate in the concrete in comparison with the bottom ash. Between pH 12-10, the increased Ba leaching may also be affected by the dissolution of ettringite from the cementitious matrix, stimulating solubility. Hence, at lower pH < 10, barium release further increases and it is assumed that the leaching of Ba is controlled by the solubility of barium sulfate [55,56].

As for copper, the leaching pattern for all three materials is more or less similar, albeit that the availability of Cu is substantially lower in the concrete in comparison with the bottom ash. The leaching of Cu from the bottom ash fractions (BMF and BGF), between pH 6 and 10, is mainly controlled by the formation of copper hydroxide (Cu(OH), ,Klemm, 1998) and the complexation to dissolved organic matter [52,58,59]. In addition, the BGF containing concrete seems to indicate a somewhat elevated Cu release between pH 6 and 10, which is the typical pH range where the binding of Cu to organic ligands is important. Possibly, the increased Cu leaching could be caused by the addition of the organic fatty acid based super plasticizer (SP) during the concrete production process. This SP contains reactive organic molecules with probably a high proportion of negatively charged carboxylic groups. Copper has a high affinity for organic ligand complexes with these carboxylic groups (fulvic acids). Overall, the results show that Cu leaching of BGF is significantly lower than the regulatory limit value and is strongly reduced compared with that of BMF. This effect is caused by the washing step where a substantial fraction of the dissolved organic carbon (DOC) fraction (humic and fulvic acids) was removed. Pilot results show that DOC reduces more than 50 % from 100-130 mg.kg dm from initial BMF input (2-31.5 mm) to 25-50 mg.kg dm in the washed BGF 2-16 mm (mixture of BGF 2-8 mm and 8-16 mm).

The leaching of Sb from BGF as a function of pH reflects the typical behavior of an oxyanion with relatively pH independent leaching at neutral (pH 7) to alkaline pH (12), which is opposite of most cations [44]. Antimony leaching from bottom ash is not yet completely understood. However, multiple possible reaction mechanisms affecting Sb leaching are described [44,47] and the extent to which these properties are dominant will most likely determine the net leaching behavior. Dissolved Sb is assumed to be predominantly Sb(V) in weathered ashes (pH range 8 to 10) and Sb(III) in fresh produced ashes at pH > 10 [47]. These forms of Sb behave differently with respect to conditions in the bottom ash, e.g. pH, DOC, Ca and Fe/Al containing minerals/ oxides [28,44,47]. Additionally, pH-dependence data for the treated BGF fraction (blue triangle data points) show that the washing and wet separation step strongly reduces Sb leaching at the natural to moderately high pH of the bottom ash granulate (pH 8.5-12).

This result indicates that part of the abundant Sb in the ash is present in soluble form that is removable by washing techniques. It has been suggested that Sb(III) can form complexes with DOC in bottom ash [47,60]. It should be noted that the leaching at pH 8.5 can remain critical after wet processing of the bottom ash into BGF.

The leaching of Sb in concrete seems to be significantly further reduced by cement use. This effect is partly caused by dilution of 50 % of total aggregate replacement. Furthermore, the relatively low Sb leaching at high >pH 11 in concrete seems to indicate that Sb is incorporated in ettringite or possibly romeite, which is typical for cementitious matrices [47,56,61,62]. In addition, ettringite and romeite stability is related to pH and start to dissolve towards lower (pH < 10.5). This process can initiate Sb release [44,47,55,57,61] as seems to be consistent with the results shown in Figure 6.8c. In summary, the Sb leaching of BGF is still critical towards the limit values of the SQD, although the emission from crushed concrete is significantly lower than the regulatory limit value.

The availability of sulfate within the bottom ash fractions is substantially reduced by the wet separation step (BGF) and to a lesser extent by dry (BMF) treatment of bottom ash. The sulfate leaching is almost pH independent over a wide range of pH values. It has been found that the leaching of sulfate from bottom ash is primarily controlled by the solubility of gypsum [20,32,37,44] and the results in Table 6.3 are consistent with these observations. Especially for sulfate, the leaching behavior of the concrete differs substantially compared with that of bottom ash. It is assumed that the leaching of sulfate in the concrete is controlled by increasing decomposition of ettringite (between pH 10-12) and the observed solubility increase results in the release of mono-sulfate [55,57,62,63].

The results of the pH dependent leaching tests also clearly indicate that the enhanced leaching of sulfate from the bottom ash containing concrete is primarily caused by the concrete and the use of cement (related to anhydrite content of cement used as setting retarder Table 6.2). However, further quality improvement to reduce SO_4 leaching from crushed concrete should aim specifically at the cement, since this material is the main source of sulfate.

The same observation is made for the pH dependent leaching of chromium (Figure 6.8). Untreated and treated bottom ash fractions show a different Cr leaching pattern, in the pH range from about 7-11, in comparison with the BGF containing concrete. The results indicate that Cr(VI) may be present in the concrete, as was also shown by earlier work on the characterization of cement mortars [55]. From this study it was also found that Cr leaching emissions levels, are related to the cement type that was used. Pure Portland cement shows the highest Cr leaching, while blended Portland cements (CEM II and CEM III containing supplementary cementitious materials) show decreasing Cr levels, all in the pH range of 7-11 [55]. However, the results of the analyzed BGF containing concrete cannot be completely explained based on the results of this research. In this

study, a CEM III with a composition of moderate 40-60 % clinker and moderate 60-40 % GGBS was used. This type of cement mortar has shown a relatively low to moderate Cr leaching (\pm 0.1 to <0.01 mg.kg at pH 5-10), where concentration is related to the clinker content [55]. Possibly, the bottom ash can exhibit some oxidizing properties causing the conversion of Cr(III) to Cr(VI) in the products. This potential effect should be studied in further work.

To finalize, the leaching behavior as a function of pH does also indicate possible expected changes in the emission of contaminants in multiple life phases, as the pH of alkaline materials tends to neutralize as a result of carbonation. This process will proceed much faster when the surface area of the material is increased in the case of granular demolition material. The pH test can be used as a basis for judgement of potential longterm weathering effects on the emission of contaminants. Further research is necessary to assess the possible scenarios in multiple life phases of construction materials and the expected degree and rate of weathering that will occur. It should be noted that, apart from the assessment of emissions to soil and groundwater, the physical properties of construction materials are also important and can as well contribute to decisions on future applications in multiple life phase.

7 Conclusions

A novel treatment process of MSWI bottom ash is developed to gain a higher level of its re-use as secondary granulate material (BGF) within earth-moist cement mixtures. A comprehensive overview demonstrates the production, design and characterization of BGF, e.g. their physical and chemical properties and related performance within a granular (open) and monolithic (concrete) application. This study leads to the following conclusions:

- The design and development of an MSWI bottom ash treatment process should focus fully on the desired granulate (end-product) properties and its final application, gaining a reliable and optimal performing granulate.
- A wet (water washing) treatment in addition to or compared with dry treatment enables the significant removal of unwanted substances within bottom ash, e.g. soluble salts (chloride and sulfate), heavy metals and organic structures as well as unwanted fine and unburned particles. Additionally, the wet treatment is an ideal process for effectively tuning and adjusting needed BGF particle-size distribution.
- BGF fractions are in compliance with the standard EN 12620 (aggregates for concrete) and do not show large variations when compared with natural aggregates. The physical and chemical properties of BGF differ slightly compared to natural gravel (e.g. lower density material ± 2400 kg/m³ instead of 2600 kg/m³, higher water absorption; 6.8 % instead of 1.3 %, and lower crushing resistance of 31-33 instead of > 35 (LA index).

- The leaching of BGF 2-8mm and 8-16mm were not fully in compliance with the open (granular) application criteria of the Dutch Soil Quality Decree (SQD). Release of chloride and antimony are just above or just below their limit values. An additional wet treatment optimization, e.g. at increased L/S ratio (extracting more soluble salts) and/or the addition of specific additives could further improve their environmental quality to comply with the SQD granular limit value [38,23].
- In two cement based earth-most concrete mixtures (pavement- and curb stones), coarse natural gravel fractions were replaced up to 100% with bottom ash granulate. Both mixtures, with increasing BGF contents, maintained necessary fresh and hardened physical and chemical performances, e.g. workability and strength, freeze-thaw limits. A moderate tensile strength increase was observed with higher BGF content within the pavement stone mixtures. Especially the BGF 2-8 mm showed promising results, where the smaller size particles have the tendency to give an overall better performance compared to the larger size fraction size 8-16 mm.
- Replacing BGF up to 100 % for natural gravel did not affect the overall emission and leaching behavior of the monolithic state concrete. The leaching behavior and analyses of granular state, crushed BGF containing concrete, within a second life phase, shows that all measured elements are far below their limit values in accordance with the SQD for granular (open) application.
- An indication of the potential emission of crushed BGF containing concrete within multiple-life phases indicated that the emissions might change in a following life phase due to weathering and carbonation. Rising sulfate (SO₄), barium (Ba) and chromium (Cr) release (by mineral dissolution and oxidation) where observed at $pH \le 10.5$. Where Cr can be attributed to the cement type and SO₄ and Ba to overall cement use; the elements are not related to the BGF content.

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CHAPTER 7

Conclusions and recommendations

1. Conclusions

This thesis contributes to an improved understanding of various physical/chemical properties and reaction mechanisms of alkali-activated and Slag cement-based (CEM III) binders and concrete mixtures, using secondary materials (i.e. slag and ashes) to produce more sustainable concrete related building materials. It also provides a better understanding of the working mechanisms and performance of a (polycarboxylate) plasticizing admixture with regard to the fresh and hardened state properties of AAM. This thesis consists of 5 main chapters, which address research that is based on involving various fundamental, experimental, practical and modelling studies. The following main conclusions can be drawn based on the outcomes and discussion of this thesis:

Working mechanism of a polycarboxylate superplasticizer in alkali-activated slag-fly ash blends (Chapter 2).

Within this detailed study, the effects of a plasticizing admixture (polycarboxylate type) on the fresh and hardened material state of an alkali activated GGBS-PCFA system were investigated.

The admixture addition provides enhanced rheological properties due to adsorption and complexation mechanisms, and modifies the material microstructure development. The admixture adsorption and complexation with mainly cationic divalent ion species controls the calcium concentration in the liquid phase by forming ligands. This goes along with the increase of silicate and aluminate concentration, as both species act as negative charge balancer to the admixture (carboxylate)-calcium complexes. Further, the admixture in an alkaline paste mixture reduces the liquid demand of GGBS and PCFA, by \approx 21-25 %. The liquid demand of PCFA is approximately a factor \approx 2 lower than GGBS.

A higher admixtures content results in higher repulsive (electrostatic) forces between particles affected by a more negative zeta-potential, gaining an enhanced mixture stability. Within the first period (up to 20 min) after initial mixing, the mixture rheology (mortar slump flow) and stability (zeta potential) is further slightly modified. This is attributed to the hydroxide induced hydrolysis of the initial admixture molecular structure, causing a change of the steric molecular structure or poly-dispersion (amount, size and length), enhancing the fluidity.

Also a higher admixture dosage slows down the dissolution reaction of the precursor, mainly GGBS, due to its high adsorption capacity. Additionally, the admixture forms complexes with calcium in solution at which a higher Ca concentration, related by a higher admixture content, results in a strong inhibition of the early age microstructure and related compressive strength development. However, the mortar compressive strength significantly develops at the later age, at a higher admixture content. At 28 days the strength of admixture-containing mortar (optimum with 2-3 ml admixture) were ≈ 44 to 48 MPa, while the reference concrete was 30 MPa. This is attributed to a

significantly thicker reaction product layer, typically around GGBS particles as a result of admixture adsorption affected by calcium bridging.

Effect of admixture on the pore structure refinement and enhanced performance of alkali-activated fly ash-slag concrete (Chapter 3).

In this chapter the effects of a plasticizing admixture (polycarboxylate) on the rheological properties and hardened state performance of AAM concrete and paste mixtures were studied.

The workability of the fresh AAM concrete significantly improves from zero slump towards a maximum measurable slump value (> 250mm) with a relatively low admixture content (0.25-0.75 wt.% of the binder). The setting time of the concrete mixture is increasingly prolonged at a higher admixture content, even up to 120 min at an admixture content at 3 kg/m³. Further, the concrete compressive strength significantly increased, over time and at an increased admixture content. The 7 and 28 days compressive strengths of admixture-containing concrete (for an optimal admixture dosage (3 to 4 kg/m³)) are about 22 and 44 MPa, respectively, while that of the reference concrete are only 15 and 23 MPa, respectively.

More in detail, the pore structure of the AAM paste mixtures is strongly refined over time and at an increased admixture content, resulting in a significant decrease of the total and effective capillary porosity and reduced material permeability. Therefore, the chloride migration coefficients of admixture modified AAM concretes at the ages of 28 and 91 days, with an optimal admixture content, are about 3.0×10^{-12} m²/s and 2.6 $\times 10^{-12}$ m²/s, respectively. Further, a relationship between the Cl-migration coefficient (Drcm) and material resistivity over time is derived for the AAM concrete mixtures. Overall, the relation between the change of pore structure and related material strength and chloride ingress strongly depends on the admixture content.

Design and performance evaluation of ultra-lightweight AAM concrete (Chapter 4).

This comprehensive study addresses the design, production and performance of ultralightweight AAM concrete (ULW-AAM), as potential load bearing, thermal insulating and sustainable building material. Research targets were to develop a practical and workable concrete mixture having a compressive strength at 28 days ranging between 8 to 10 MPa, a dry density of 700 to 900 kg/m³ and a very low thermal conductivity (TC) of < 0.11 W/(m·K). As aggregate material only light-weight aggregate (LWA), known as expanded glass, was used.

Applying an optimized particle packing approach (modelling calculations) for the mixture design, improved fresh mixture stability and workability properties were obtained. By increasing the liquid dosage (140 to 175 l/m^3) which is related to a higher L/B ratio during concrete production, the mixture workability is significantly improved (slump from 10 to 280 mm). As a side effect, the concrete had a lower dry density

and reduced 28-day compressive strength, due to the increased porosity. The binder/ aggregate (B/A) ratio also greatly influenced the fresh and hardened AAM concrete performance. A higher ratio increased the compressive strength at 28 days (up to 25%) and lowers the water penetration under pressure.

When the LWA fraction of 4-8 mm is replaced by LWA of 2-4 mm, the concrete performance is positively affected. The 28 day compressive strength increased (up to 11 %) and thermal conductivity decreased (up to 27 %). The strength modification is related to the higher aggregate abrasion resistance of the 2-4 mm fraction. The decline of the TC is related to a higher concrete porosity, related to a higher material porosity of 2-4 mm fraction. Furthermore, the introduction of an air entraining agent (AEA) optimizes the mixture performance by further lowering the concrete density and the TC, initiated by the created micro air bubbles. Nevertheless, a 16 % loss of compressive strength is observed. Furthermore, a higher compressive strength of the concrete (36%) is obtained by lowering the alkali concentration from 3 to 2 M NaOH. Finally, an optimal ultra-lightweight AAM concrete is developed having a very low TC of 0.07 W/ (m·K) with a compressive strength of 8 MPa. Which indicates a great potential for the production of a load bearing and highly insulating building material as an alternative for traditional materials.

Leaching of oxyanions from monolithic and granular slag-fly ash alkali-activated materials as a function of the mixture composition *(Chapter 5).*

This chapter discusses the leaching behavior of single GGBS and PCFA as precursor in AAM as well as the influence of the AAM mixture design on the leaching of oxyanion metal (As, V, Se, Mo, Cr) within a granular (open) and monolithic (concrete) application. The compressive strength of monolithic state AAM strongly depends on the mixture composition by variation of: NaOH activator alkalinity, PCFA-GGBS (precursor) mass proportion of the total binder and L/B ratio. For the environmental AAM performances, the total element leaching of AAM concretes (monolithic state) was far below the Dutch regulatory leaching limit values for monolithic materials, even though AAM strongly differed in mixture composition (NaOH activator alkalinity, PCFA-GGBS mass proportion of the total binder and L/B ratio). However, the leaching of AAM aggregates (granular state) strongly depends on the mixture design. The release of As and V increases with a higher L/B ratio and a higher activator molarity (2 till 5 M NaOH); the leaching of As, Mo, Se and V strongly increases at an increased PCFA content for different PCFA-GGBS precursor/binder compositions. A higher PCFA content significantly increases and a higher GGBS significantly decreases the leaching of As, Se, V, Mo and Cr from granular state AAM. This is explained by the oxyanion content and leaching, within a natural and or highly alkaline aqueous environment, which is for PCFA much more significant for As, Se, V, Mo and Cr in comparison with GGBS, which mainly contains and releases V.

AAM aggregates meet the Dutch SQD leaching limits for open application of granular building materials when the PCFA content of the total binder composition is not higher than 30 wt.%. The leaching of AAM aggregates has been tested (pH- dependent test) to identify and simulate pH lowering due to potential carbonation processes. Leaching of Mo, Se, and Cr are, more or less, insensitive to pH lowering (pH range 13 to 8), although the leaching of V decreases at decreasing pH value. The overall oxyanion behavior and concentrations fit relatively well within the 5% and 95% percentile leaching range of blended (slag and fly ash) Portland cements. However, the leaching of V and As from AAM aggregates is slightly higher at high pH (> pH 11) compared to blended Portland cementitious materials. Although, the results indicate that an increase of the GGBS of binder content decreases leaching. Overall, the obtained understanding of the oxyanion leaching behavior is crucial to design new AAM (concrete) structures and building materials using secondary materials that meet the regulatory leaching limits, both for initial use (monolithic) and at the end of the service life after demolition (aggregate).

High performance of treated and washed MSWI bottom ash granulates as natural aggregate replacement within earth-moist concrete *(Chapter 6)*.

This comprehensive study discusses and demonstrates the production, design and characterization of MSWI bottom ash (BA) granulates, e.g. their physical and chemical properties and related performance for granular (open) and monolithic (concrete) applications.

A wet (water washing) treatment in addition to/or compared with dry treatment enables the significant removal of unwanted substances within BA, e.g. soluble salts (chloride and sulfate), heavy metals and organic structures as well as unwanted fine and unburned particles. Additionally, the wet treatment is an ideal process for effectively tuning and adjusting the needed granulate particle-size distribution. The produced BA granulate fractions (2-8 mm and 8-16 mm) were in compliance with the standard EN 12620 (aggregates for concrete);variations were comparable with natural aggregates. Further, the leaching of both BA granulate fractions were not fully in compliance with the open (granular) application criteria of the Dutch Soil Quality Decree (SQD), the release of chloride and antimony are just above their limit values.

Coarse natural gravel fractions were replaced up to 100 % with BA granulate for two Portland slag cement (CEM III A) based earth-moist concrete mixtures, producing pavement- and curb-stones. Both mixtures, at an increased BA granulate content, fulfilled the necessary fresh and hardened physical and chemical requirements, e.g. with regard to workability, strength and freeze-thaw limits. For the pavement stone mixtures, even a moderate tensile strength increase was observed at increased BA granulate content. Especially, the BA granulate fraction 2-8 mm showed promising results, where the smaller size particles have the tendency to result in an overall better performance compared to the larger size fraction size 8-16 mm. Replacing natural aggregates up to 100% for BA granulates did not affect the overall leaching and the related element leaching behavior of the monolithic state concretes. Additionally, leaching in the granular state (concrete containing crushed BA granulates), at the end of their service life) shows that all measured elements are far below their limit values in accordance with the SQD for granular (open) application. Finally, an indication of the potential leaching of the recycled aggregate fraction within multiple-life phases is performed. The leaching of recycled aggregate of concrete with a up to 100% gravel replacement by BA granulate, might change in a following life phase due to weathering and carbonation (pH lowering). Typically, rising chromium, sulfate and barium releases (by mineral dissolution) was observed at pH \leq 10.5. The source of the increased chromium leaching behavior can be attributed to the cement type and that of sulfate and barium leaching, to the overall Portland cement use. These elements are not related to the bottom ash granulate content.

2. Recommendations for future research

Additional research is required from a scientific point of view, to gain a better understanding of the underlying working mechanisms and processes dealt with within the framework of this thesis. The main recommendations of this thesis are the following:

- A relatively small dosage of a well performing plasticizing admixture can significantly modify the fresh and hardened state properties of AAM. However, more detailed chemical analysis needs to be executed on the working mechanism of plasticizing admixtures (i.e. polycarboxylate and other molecular types) in AAM systems. Firstly, research should focus on the admixture its backbone structure (i.e. length and molecular structure) which is of strong influence to its adsorption and complexation reactions mechanism onto precursor particles and with dissolved element species (i.e. Al, Si Ca). Secondly, the effects of admixture use and type on the alternation of the AAM microstructure development (i.e. gel reaction mechanisms, composition, porosity and assembly effects) over time should be further analyzed. These topics are of great importance for the design more effective admixtures for AAM, as to increase the practical potential of alkali-activated binders.
- The use of admixture, affects the overall matrix and microstructure developed (i.e. composition, porosity and density) of AAM concrete. Additional microscopic research needs to performed to improve the understanding of the influence of admixture on the AAM concrete matrix and microstructure development over time. To gain more understanding between the influence ad effects of admixture use and the physical/ chemical material (durability) performance of AAM concrete over time.

- A highly potential ultra-lightweight AAM (ULW-AAM) concrete mixture was developed having a very low thermal conductivity of 0.07 W/(m·K) with a compressive strength of 8 MPa, which indicates a great potential for the real life production of a load bearing and highly insulating building material as an alternative for traditional materials. Additional research on the mixture design, needs to identify the effects and influence other dominant system parameters (e.g. activator concentration and a different (GGBS-PCFA) binder composition), in order to develop even more advanced sustainable ultra-lightweight mixtures, with different properties and new functional practical applications.
- Leachable concentrations of oxyanions from AAM (granular and monolithic material state) are strongly influenced by the binder (PCFA and GGBS) composition. By optimizing (increasing) the GGBS binder content in the mixture, a strong reduction of overall heavy metal leaching is obtained. However, further experimental research in combination with geochemical modeling should be done, in order to gain an improved understanding of the underlying physical/chemical processes (adsorption and complexation mechanisms) that control heavy metal (cat- and anionic) element leaching from granular and monolithic state AAM. To gain an improved understanding about the leaching dynamics of AAM and the controlling factors, as to compare this with traditional binder systems and the regulatory leaching limits for building materials.
- The leaching of dry and wet treated bottom ash granulates still does not fully comply with the open application criteria for granular building materials of the Dutch Soil Quality Decree (SQD). However, the wet treatment significantly improves (lowers) the overall leaching of potential toxic elements (salt and heavy metals) from bottom ash granulate. Additional research should be done specially on the wet treatment optimization, e.g. at increased L/S ratio (extracting more soluble salts such as chloride and sulfate) and the addition of specific complexation additives. This further improves the environmental quality of BA granulates, by reducing heavy metal leaching mainly that of antimony and copper, to finally comply with the regulatory leaching limit value.

ABBREVIATIONS AND SYMBOLS

AAM	Alkali Activated material
AEA	Air Entraining Agent
Ad	Admixture
Al	Aluminium
As	Arsenic
Ba	Barium
BA	Bottom Ash
BGF	Bottom ash Granulate Fraction
BMF	Bottom ash Mineral Fraction
Br	Bromide
Ca	Calcium
Cl	Chloride
Со	Cobalt
CO ₂	Carbon dioxide
CO	Carbonate
Cr	Chromium
CS	Curbstone
Cu	Copper
D ₅₀	Average particle size of 50% of the total mass [µm]
D	Diffusion
Drcm	Diffusion coefficient Rapid Chloride Migration [×10 ⁻¹² m ² /s]
DOC	Dissolved Organic Carbon
CEM	Cement
CEM III	Cement that contains a high content of slag
CASH	Calcium Aluminate Silicate Hydrate
EC	Electrical Conductivity [µS/cm]
EDX	Energy-dispersive X-ray spectroscopy
ESEM	Environmental Scanning Elecrton Mircoscope
E	Deformation coefficient
\mathbf{F}^{r}	Fluoride
Fe	Iron
g	Gram
GGBS	Ground Granulated Blas furnace Slag
h	Hour
Hg	Mercury
HNO ₃	Nitric acid
H ₂ O	Water
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry

ITZ	Interfacial Transition Zone
К	Potassium
Kg	Kilogram
LOI	Loss Of Ignition at 950 degree Celsius
LWA	Light Weight Aggregates
MB	Mineral blended Binder
Mg	Magnesium
mm	Millimeter
Mn	Manganese
Mo	Molybdenum
min	Minute
MIP	Mercury Intrusion Porosity
MPa	Mega Pascal
MSWI	Municipal Solid Waste Incinerator
ml	Milliliter
Na	Sodium
NaOH	Sodium Hydroxide
NASH	Sodium Aluminate Silicate Hydrate
NEN	NEderlandse Norm
NEN-EN	NEderlandse Norm- European Norm
Ni	Nickel
Р	Phosphor
Pb	Lead
PC	Portland Cement
PCE	Polycarboxylate
PCFA	Pulverized Coal Fly ash
pН	Acidity or basicity of an aqueous solution
ppm	Parts Per Million
PS	Pavement stone
PSD	Particle Size Distribution
RCM	Rapid Chloride migration
RH	Relative Humidity
RPM	Rotations Per Minute
Sb	Antimony
Se	Selenium
Si	Silicon
Sn	Tin
S	Sulfur
SO ₄	Sulfate
SP	Superplasticizer

SQD	Soil Quality Decree
Sr	Strontium
Т	Time [min]
TC	Thermal conductivity [W (m.K)]
TCC	Total Carbon Content
TEM	Two Electron method
TGA	Thermal Gravimetric Analysis
Ti	Titanium
ULW-AAM	Ultra-Lightweight Alkali Activated material
ULW-PC	Ultra-Lightweight Portland Cement
V	Vanadium
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
Zn	Zinc
B/A	Binder to Aggerate
v/v%	Volume percentage
Kg/m ³	Kilogram per cubic meter
L/B	Liquid to binder ratio
L/m ³	Liter per cubic meter
L/S	Liquid to Solid
N/mm ²	Newton per square millimeter
mg.kg dm	Milligram per Kilogram of Dry Matter
m ² /s	Square meter per second
W/C	Water to binder ratio
wt.%	Weight percentage
ρ.	WZ
pp	Water demand
M	Molar No. 1
V	Volume
μm	
٨	Inermal conductivity $[W/(m.K)]$
ç	Density [kg/m ²]
с С	Zeta potential [mV]
Ωm	Kesistivity

LIST OF PUBLICATIONS

Journals

- Keulen, A., Kakebeeke, P.I.J., Justnes, H., Yu, Q.L. (2017). Working mechanism of a polycarboxylate superplasticizer in alkali-activated slag-fly ash blends *(Publication in progress).*
- Keulen, A., Dijkstra, J.J., A., Zomeren, A. Van, (2017). Leaching of oxyanions from monolithic and granular slag-fly ash alkali activated materials as a function of the mixture composition (*Publication in progress*).
- Keulen, A., Yu, Q.L., Y, Zhang, S., Grünewald, S. (2017). Effect of admixture on the pore structure refinement and enhanced performance of alkali-activated fly ash-slag concrete (*Construction and Building Materials 162, 2017, pag. 27-36*).
- Zhang, S., Keulen, A., Arbi, K., Ye, G. (2017). Waste glass as partial mineral precursor in alkali-activated slag/fly ash system (*Cement and Concrete research 102, 2017, pag. 29-40*).
- Florea, M.V.A., Doudart de la Gree, G.C.H., Keulen, A., Brouwers, H.J.H. (2016). Contaminated Biomass Fly Ashes-Characterization and Treatment Optimization for Reuse as Building Materials (*Waste Management, 49, 2016, pag. 96-109*).
- Keulen, A., Zomeren, A. Van, Harpe, P., Aarnink, W., & Simons, D.J., Brouwers, H.J.H. (2016). High performance of treated and washed MSWI bottom ash granulates as natural aggregate replacement within earth-moist concrete (*Waste Management 49, 2016, pag. 83-95*).
- Huiskes, D.M.A., Keulen, A., Yu, Q. L., Brouwers, H.J.H. (2015). Design and performance evaluation of ultra-lightweight geopolymer concrete (*Materials and Design 89, 2016, pag. 516-526*).

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Conference proceedings

- Keulen, A. (2017). Physical and chemical performance of treated MSWI bottom ash (fine fraction) as sand replacement in concrete, 5th International Slag Valorisation Symposium, Leuven, Belgium.
- Keulen, A. (2016). Inorganic polymer production and characterization, using industrial 'waste' materials. GMI Ash Trade Europe, Rome, Italy.
- Keulen, A., (2016). Design and performance of geopolymer concrete applications. RILEM TC DTA Workshop on Alkaline-activated Materials for Construction. Delft, The Netherlands.
- Zhang, S., Keulen, A., Arbi, K., Ye, G. (2016). Characterization and preliminary processing of biomass ash for possible utilization in alkali-activated materials. The 3rd International RILEM Conferences on Microstructure Related Durability of Cementitious Composites. Nanjing, China.
- Arbi, K., Nedeljkovic, M., Zuo, Y., Grünewald, S., Keulen, A., & Ye, G. (2015). Experimental study on workability of alkali activated fly ash and slag-based geopolymer concretes. Geopolymers: An ECI Conference, Herrnstein, Austria.
- Zhang, S., Keulen, A., Arbi, K., Ye, G. (2015). Waste glass powder as partial binder precursor in Fa/BFS geopolymer paste. Geopolymers: An ECI conference, Herrnstein, Austria.
- Huiskes, D. M. A., Keulen, A., Yu, Q. (2015). Design and performance evaluation of ultra-lightweight geopolymer concrete. 19th Ibausil. Wiemar, Germany.
- Keulen, A., Zomeren, A. Van, Harpe, P., Aarnink, W., Simons, D.J. (2015). Characterization and performance of treated and washed MSWI bottom ash granulates as natural aggregate replacement within earth-moist concrete. 19th Ibausil. Wiemar, Germany.
- Nugteren, H., de Groot, Y., Weststrate, R., Yliniemi, J., Keulen, A., Meesters, G. (2014). Granulation of Industrial by-products and waste with geopolymer binders. 14th CIMTEC, Italy.
- Keulen, A., Florea, M.V.A., Brouwers, H.J.H. (2012). Upgrading MSWI bottom ash as building material for concrete mixes. 18th Ibausil. Wiemar, Germany.

• Florea, M.V.A., Keulen, A., Brouwers, H.J.H. (2011). On the application of MSWI bottom ash as aggregate replacement in concrete mixes. Eurasia waste management symposium, Istanbul, Turkey.

Patents (as inventor):

- Pozzolanic binder composition (2008): 2002282 NL (active).
- Werkwijze voor het stabiliseren en immobiliseren van anorganische zoute stromen/ afvalstoffen (2009): Part I : 1036620 NL (active) and Part II : 1037744 NL (active).

CURRICULUM VITAE

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Work-experiences

1	
2007 till now	: Project Manager Science & Technology at Mineralz (part of Renewi),
	The Netherlands.
2011 till now	: Manger R&D at SQAPE Technology (joint venture of Van
	Gansewinkel & Cementbouw), the Netherlands.
2006-2007	: Project leader R&D at Insulinde Recycling en Milieu BV (part of
	Attero Group), Amsterdam, The Netherlands.
Studios	
Studies	
2012 -2017	: Ph.D. Candidate, Department of the Built Environment, Eindhoven
	University of Technology, The Netherlands.
2004-2006	: Master study (MSc.) Sustainable development/ Environmental
	Sciences, Department Geosciences, Utrecht University, The
	Netherlands.
1999-2004	: Bachelor study (BSc) Environments sciences, specialisms Integral
	soils and water management, and remediation technologies, Van Hall
	Institute the Netherlands.

This thesis addresses the use of secondary minerals (slags and ashes) and a plasticizing admixture in environmentally friendly cement based alkali activated systems for the production of 'sustainable' building materials with improved technical and 'environmental' performance. The main research topics are divided in:

Technical performance:

- Development of an alkali activated slag-fly ash binder system in combination with a plasticizing admixture, to improve the fresh (e.g. rheology and slump) and hardened (e.g. strength, porosity, chloride migration) properties of alkali activated concrete mixtures.
- Investigation on the working mechanism and influence of a polycarboxylate admixture alkali activated in slag-fly ash mixtures.
- Design and performance evaluation of ultra-lightweight alkali activated slag-fly ash concrete.
- Assessment of treated MSWI bottom ash and secondary aggregate, to replace coarse primary aggregate, in the production and design of blast furnace slag cement concrete mixtures.

Environmental performance:

- Evaluation of leaching behavior and mechanisms of heavy metals and salts of secondary minerals (ground granulates blast furnace slag, fly ash and untreated and treated MSWI bottom ash fractions) in natural and alkaline environment.
- Assessment of leaching behavior and mechanisms of metal oxyanions of alkali activated slag-fly ash materials and influence of the mixture design, in relation to monolithic (i.e. concrete) and granular (i.e. aggregate) state materials.
- Assessment of leaching behavior of heavy metals and salts of blast furnace slag cement materials, replacing natural aggregate with treated MSWI bottom ashes from monolithic (i.e. concrete) and granular (i.e. aggregate) state materials.
- Modeling of pH dependent leaching behavior of heavy metals and salts of granular state materials, as aggregates in their second life phase when concrete products are recycled.

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