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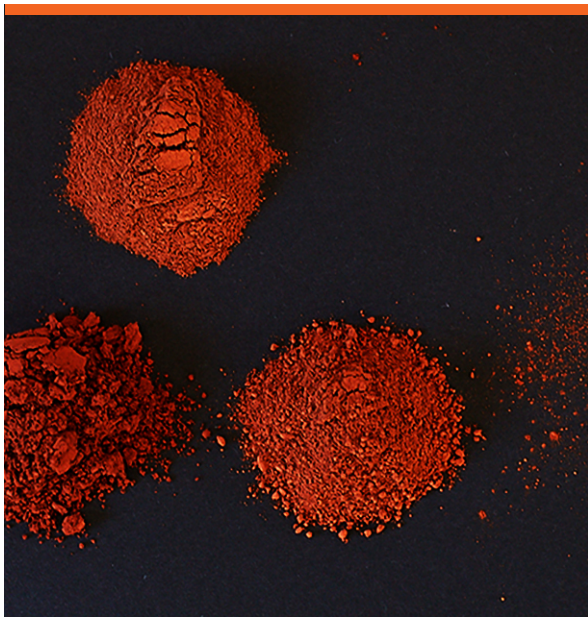

Annemette Kappel

PhD Thesis

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Alternative Ashes in Concrete

New Aesthetical and Technical Performance

PhD Thesis

Annemette Kappel June 2017

Technical University of Denmark

Department of Civil Engineering

PREFACE

This PhD thesis is the outcome of my research carried out at the Department of Civil Engineering at Technical University of Denmark (DTU BYG) between Dec 2012 and June 2017, where I was affiliated as PhD student. The main supervisor was Professor Lisbeth M. Ottosen from DTU BYG, and Associated Professor Gunvor M. Kirkelund, Professor Per Goltermann also from DTU BYG and Anja Bache PhD and Artist were my co-supervisors. The PhD thesis is based on three scientific papers and one conference paper in which I am the first author. The conference paper and the three scientific papers are enclosed in chapter 5 in the thesis.

The research presented in the thesis is intended for professionals and researchers who have an interest in the overall topic *Waste as resource* and specifically in utilisation of sewage sludge ash as resource in building materials. Research focus was centered on the aesthetical and technical potentials when sewage sludge ash is used as partial cement replacement in mortar. The aim of the research was to provide knowledge relevant for different disciplines of engineering, architecture and design, which can be used to evaluate potentials and constrains of utilising sewage sludge ash as resource for production of concrete in the future.

ACKNOWLEDGEMENTS

I wish to acknowledge Technical University of Denmark for funding the PhD study and express my gratitude to my supervisors Professor Lisbeth M. Ottosen and Associate professor Gunvor M Kirkelund for excellence guidance, support and encouragement during the entire period of the project. Furthermore, I will like to thank my colleges in the *ZeroWaste Byg* group especially my fellow PhD students – Wan Chen and Barbora Krejcirikova. Thank you for cooperation on organizing the *ZeroWaste Byg* seminars held in the period of autumn 2014 to fall 2015. I have learned a lot especially from the discussions we had. I will also like to give my thanks to my colleges at Section for Arctic Engineering and Sustainable Solutions, especially Raimon Parés Viader and Krzysztof Piotr Kowakski for collaboration in the planning, designing, and running a series of Electrodialytic experiments by which we managed to produce sufficient amount of phosphorous extracted sewage sludge ash intended for further investigations as cement replacement in mortar. Without this it wouldn't have been possible for me to achieve the tasks of the research which I had planned. I would also like to express my gratitude and appreciation to concrete technician Per Leth for always being very kind to assist me in the concrete lab; laboratory technicians Ebba Cederberg Schnell, Sabrina June Hvid and Malene Grønvold for carefully conducting the chemical analyses. At last but not the least I would like to thank my family- Jesper, Venke and Molly. Thank you for your unconditional support and love –or simply, thank you for being you.

ABSTRACT

The research findings presented in this thesis *Alternative Ashes in Concrete – New Technical and Aesthetical Performance* contribute to the discussion on utilisation of sewage sludge ash (SSA) as a secondary resource. SSA is the result of incineration of sewage sludge, which is mainly applied at water treatment plants in dense areas to safely handle large amount of sludge. Today SSA is in most cases sent to landfill, which raises the question: is it possible for SSA to change status from waste to resource by utilising SSA in the production of cement based materials?

So far SSA has not commercially been applied in concrete production. This is even though research has shown that SSA has some potential as secondary resource to partially replace cement in blended cements or concrete. One main reason might be the fact that SSA has a relatively high content of phosphorous, which is an irreplaceable nutrient essential for crop growth. Since phosphorous is regarded as a scarce resource, options to keep phosphorous in the nutrient cycle are increasingly becoming an object of attention. Consequently, the present research has focused on SSA utilisation as resource for production of cement based materials without losing the potential source for phosphorous used in fertilizer production.

The present research included three studies in which different degrees of processed SSA was used in mortar to partially replace cement. The three processes used to treat the SSA were: milling, acid washing and electrodialytic treatment. The treatments were applied for two purposes: 1. optimizing the performance of the mortar, and 2. to recover the phosphorous available in the SSA. The main purpose of the experimental work was to unfold the aesthetical and technical potentials of mortar with SSA by showing how basic properties of mortar were affected when 20 % of cement was replaced with untreated and treated SSA.

The outcome of the research project has both a linguistic and non-linguistic part, which collectively forms the thesis of a practiced based research. The non-linguistic part of the thesis is represented by four series of physical samples that show how ordinary mortar transforms when different degrees of processed SSA are used as partial cement replacement. The physical output signifies the potentials of using SSA as a resource, whereas the technical and aesthetical potentials are unfolded by correlating the physical output with

quantitative measurements of compressive strength and flow value of the mortars. The research covers a general assessment of the feasibility to utilise SSA-containing concrete, and the experiments were designed to investigate the material behaviour in an open framework.

The research findings of the present study support findings of previous research. Numerous studies have shown that the compressive strength and workability decrease when SSA is used as partial cement replacement in mortar and concrete. However, when SSA is milled to obtain finer particles it is possible to reach compressive strength and flow value comparable to ordinary mortar. Up until now only one previous study has combined phosphorous recovery and an investigation of phosphorous extracted SSA in mortar, and only one previous demonstration project *Biocrete* has reported on the influence of SSA on the colour of concrete. Therefore have I chosen to focus on these two parameters in order to address these issues that challenge the use of SSA as resource in cement based materials.

The experimental work of the present research showed that the colour intensity increased parallel to an increase of the compressive strength and workability when the particle sizes of raw SSA decreased (obtained by increasing durations of milling). Furthermore, it was shown that the properties of mortar were notably affected when phosphorous was extracted before the SSA was used in mortar as partial cement replacement. Especially the visible changes were even more evident for mortars with SSA after phosphorous extraction, both acid washed and electrodialytic treated. The colour of mortar with either acid washed SSA or electrodialytically treated SSA changed from the familiar grey colour of ordinary mortar into two similarly saturated reddish colours. The colour tones of the mortar did not gradually increase when the two types of treated SSA were milled to obtain finer particles as seen for raw milled SSA. The compressive strength found for mortar with acid washed SSA was slightly below the compressive strength of ordinary mortar, but increased when the treated SSA was milled to finer particle sizes and reached to the level of the reference. Like the compressive strength the workability increased, however, without reaching the level of ordinary mortar. For mortar with electrodialytically treated SSA, the milling of the treated SSA did not have any significant effect on the performance of mortar, which initially was below ordinary mortar.

The findings of the present research can be used to point out future possibilities to utilise SSA as resource in cement based materials in specific cases by displaying the behaviour of mortar with the different types of processed SSA. The knowledge obtained is attended for professionals from different disciplines in engineering and architecture and the result of the research may serve as common ground for future research on SSA utilisation within the scope of resource efficiency.

SAMMENFATNING

Dette ph.d. projekt *Alternative asker i beton – ny teknisk og æstetisk performance* er et bidrag til diskussionen omkring anvendelse af slamaske som en sekundær ressource. Slamaske stammer fra afbrænding af slam, som er en metode, der anvendes til at reducere mængden af slam fra spildevandsrensning. I dag bliver slamaske som oftest deponeret, og derfor rejses spørgsmålet: kan slamaske ændre status fra affald til ressource ved at anvende slamaske i produktionen af cement baserede materialer?

På trods af at en række forskningsresultater har vist, at slamaske har potentiale til at kunne anvendes som delvis cement erstatning i beton, har dette endnu ikke ført til, at slamaske udnyttes kommercielt. En væsentlig årsag kan være den, at slamaske har et højt indhold af fosfor, som er et vigtigt næringsstof uundværligt for alle levende organismer. En stor del af den fosfor, som i dag anvendes i gødning, kommer fra minedrift af fosfat. Da disse fosforressourcer i realiteten anses for knappe, er der en stigende interesse for at udvikle nye metoder, der tillader at fosforen forbliver i næringskredsløbet tilgængelig for landbruget. I dette forskningsprojekt er fokus derfor rettet mod at undersøge brugen af slamaske som delvis cementerstatning i beton, for samtidig inddrage det forhold at slamaske er en vigtig ressource for fosfor, som derfor ekstraheres før asken anvendes i beton.

Forskningsprojekt består af tre adskilte studier, hvor anvendelse af både ubehandlet og behandlet slamaske er blevet undersøgt som delvis cementerstatning i mørtler. Behandlingsmetoderne, der er blevet anvendt, er: 1. formaling af asken, 2. syrevask og 3.elektrodialytisk behandling. Formålet med at anvende disse metoder var at forbedre de undersøgte materialegenskaber for mørtlerne, og at udvinde fosforen fra slamasken inden den videre anvendes som cementerstatning. Hovedformålet med det eksperimentelle arbejde var at udfolde potentialerne for mørtler med slamaske ved at undersøge, hvordan grundlæggende materialeegenskaber såsom farven og styrke reagerede, når 20 % af cementen blev erstattet med henholdsvis ubehandlet og behandlet slamaske.

Ph.d projekt består både af en verbal og non-verbal formidling af forskningsresultaterne, som samlet set udgør et praksisbaseret forskningsprojekt. Den non-verbale formidling består af fire serier af

materialeprøver, som viser hvordan mørtelen transformeres, når forskellige grader af forbehandlet slamaske bruges som cementerstatning. Det fysiske output har til formål at udpege materialets æstetiske potentiale og sammenstille dette med kvantitative egenskaber som f.eks. trykstyrke og bearbejdelighed. Formålet er derigennem at anskueliggøre de muligheder som opstår, når slamaske anvendes som ressource i cementbaserede materialer. Forskningsresultatet indbefatter en generel vurdering af de potentialer og begrænsninger, som er forbundet med brugen af slamaske i mørtler.

Forskningsresultater fra tidligere studier viser at trykstyrke og bearbejdelighed reduceres, når slamaske anvendes som delvis cementerstatning i beton og mørtler. Formales slamasken derimod til finere partikelstørrelser, er det muligt at opnå trykstyrke og bearbejdelighed, som er sammenlignelige med almindelig mørtel. Eksperimenter fortaget i forbindelse med dette forskningsprojekt understøtter disse tidligere resulter. Men indtil nu har kun et enkelt studie undersøgt brugen af slamaske, hvor fosforen er fjernet inden videre brug i beton. Derudover har slamaskens indvirkning på mørtlens farve ikke tidligere været direkte genstand for en undersøgelse, og kun et enkelt dansk demonstrationsprojekt *Biocrete* har rapporteret at farven påvirkes, når slamaske indgår som en del af betonens bestanddele. Derfor har jeg med dette projekt valgt at inddrage disse to parameter for at adressere udfordringerne som knytter sig til slamaske som ressource.

Resultaterne af studierne viser, at når slamasken bliver formalet til finere kornstørrelser, så intensiveres farven gradvist parallelt med, at trykstyrken stiger og bearbejdeligheden for mørtlerne forbedres. Derudover viser resultaterne også, at materialeegenskaberne for mørtlerne ændre sig betydeligt, når slamasken enten er blevet syrevasket eller elektrodialytisk behandlet for at ekstrahere fosforen. Disse to metoder havde begge en afgørende betydning for mørtlens visuelle fremtoning, som ændrede sig fra den grå velkendte farve til mere mættede rødlige nuancer. I forhold til de udvalgte parameter har formalingen en større betydning for den ubehandlede slamaske. Trykstyrken for mørtlerne med syrevasket aske var som udgangspunkt sammenlignelig med referencen, mens den for mørtler med elektrodialytisk behandlet aske var mindre. Formaling af disse to typer asker havde ikke større betydning for trykstyrken. I modsætning til trykstyrken

forbedredes bearbejdeligheden for mørtlerne med syrevasket slamaske igennem formalingen, mens dette ikke havde nogen effekt for mørtlerne med formalet elektrodialytisk behandlet slamaske.

Forskningsprojektet bidrager med ny viden i forhold til, hvordan de fosforekstraherede slamasker indvirker på mørtlernes generelle egenskaber både æstetiske og tekniske. Resultaterne kan bruges til at udpege anvendelsesmuligheder af cementbaserede materialer med slamaske og bruges som grundlag for nye projekter, hvor slamasken som ressource testes i beton i forhold til specifikke formål.

CONTENT

1. INTRODUCTION

This PhD thesis *Alternative Ashes in Concrete – New Technical and Aesthetical Performance* discusses potentials connected to the use of sewage sludge ash (SSA) as partial cement replacement in cement based materials. The project was conducted as part of *ZeroWaste Byg* which is a research initiative taken in 2012 at the Department of Civil Engineering, Technical University of Denmark. The goal of *ZeroWaste Byg* is to develop the research area and compile knowledge on *waste as resource* when these secondary resources are used in production of construction materials. The research focus of *ZeroWaste Byg* described prior to the start of present research project filled out the roll as the programmatic setting of the research and the experimental work initiated to search for new potentials of cement based materials with SSA.

> *"The research aims at placing the build environment centrally in a sustainable material cycle of society. Research and innovation focus is on increased replacement of natural raw materials with secondary resources (if necessary optimized). In addition, strong emphasis is on utmost recycling at the end of life. Such redesigned construction materials strongly support waste minimization in society, as the building industry is a major materials consumer on a volume base.* "(ZeroWaste Byg n.d.)

SSA is the particulate residue produced at wastewater treatment plants where thermal processing of sludge is applied. The main purpose of incinerating sludge is to reduce the volume and to prevent spreading of contaminates as heavy metals and pathogens (Fytili & Zabaniotou 2008; Lofrano & Brown 2010). Today SSA is regarded as waste and in most cases SSA is landfilled (Donatello & Cheeseman 2013). In order for SSA to obtain the status as resource, it requires that appropriate use is found.

Over the last 30 years utilisation of SSA has been studied, mainly as partial cement replacement in cement based materials, but also in production of construction materials and products in general (Donatello &

Cheeseman 2013). The practice of utilising waste materials, residues and by products from other sectors in concrete or as component in blended cement is not new. Cement and concrete producers have in the role as scavengers benefited economically by utilising by-products from other industries in production of cement and concrete (Reijnders 2007). Residues such as coal fly ash and by-products as blast furnace slag or silica fume have been found useful and can be used to replace cement in concrete in quantities between 20 – 70 % material (Mehta et al. 2014). When secondary resources are used as partial cement replacement, the generic term used for these types of materials is supplementary cementitious material (SCM) (Snellings et al. 2012).

Incentives to utilise by-products and residues as SCM may initially have been a part of cost saving strategy, a strategy which however also was beneficial for the development of new concrete technologies such as high strength concrete (Mehta et al. 2014). Furthermore, utilisation of by-product as SCM in concrete have also environmental benefits when a CO_2 intensive material as cement is replaced by a less intensive such as industrial produced by-products. During cement production approximately 1 ton CO_2 per 1 ton of cement is produced. The high emission of CO_2 is due two things. At first the chemical reaction of lime during processing, and secondly the high amount of energy required to reach the temperatures necessary for producing reactive cement clinker. Therefore, if it is possible to replace cement with a waste material, the emission of CO_2 related to cement production from both can be reduced.

Focus of previous studies on use of SSA in mortar has been centred on chemical, physical, mechanical and environmental implication and changes when SSA is used as SCM. So far research has not led to a general application of SSA in concrete despite numerous studies conducted in this area. Several explanations as to why may be found. One reason is likely related to the fact that the performance of mortar and concrete is negatively affected, as the majority of studies conducted have found that the compressive strength and workability decrease when SSA is partially replacing cement. (Cyr et al. 2007; Donatello & Cheeseman 2013; Lynn et al. 2015) Another reason of importance is that SSA has a relatively high content of phosphorous.

Phosphorous is an irreplaceable nutrient essential for life and therefore also for crop growth. Currently, phosphorous input in agriculture depends on supplies of phosphate derived from phosphate rock mining. Phosphate rock is a finite resource (Cordell et al. 2009; Reijnders 2014; van Dijk et al. 2016) and the deposits of phosphate rock are unequally distributed globally, as 77% of the reserves are situated in Morocco and West Sahara (van Dijk et al. 2016), countries which can be considered geopolitically unstable. For these reasons, dependency on phosphate rock is critical, as it threatens the food supply security globally.

> *"Phosphorus governance at global, regional, and local scales is required to stimulate and support context-specific sustainable strategies to ensure all the world's farmers have sufficient access to phosphorus to feed the world and ensure ecosystem integrity and farmer livelihoods."* (Cordell & White 2014, p.161)

In the light of the phosphorous challenge, attention on resource efficient use of phosphorous is increasingly required to prevent food shortages, as it was seen in 2008. As a consequence of the financial crises in 2008, the prices on phosphate rock went unproportioned up by 800%, which meant that farmers in the developing countries couldn't afford buying fertilizer (Cordell & White 2014). For this particular reason when considering SSA as resource instead of as a waste material, the primary resource of interest is phosphorous. Thus, research in utilisation of SSA as resource is particularly interesting, because it potentially confronts two essential problems related to human activity and needs simultaneously, namely: nutrient depletion and the problems of the cement production as CO_2 intensive industry. However, until now research in utilisation of SSA as resource in concrete production has focused on SSA as partial cement replacement, except for one study by Donatello et al. (2010a), without addressing the fact that SSA is source for phosphorous. Research in this area is lacking. Consequently, in the present research project the studies conducted included experiments in which phosphorous was recovered before the SSA was tested as SCM in mortar.

2. BACKGROUND

2.1 Waste as resource

In the 5th assessment report by the *Intergovernmental Panel on Climate Change*s (IPCC) resource use efficiency is pointed out as one pathway to mitigate climate change (IPCC 2014). At the political level within the European Union (EU) resource use efficiency is in cooperated into waste management legislation by implementation of the *Waste management hierarchy* (EC 2008a). The waste management hierarchy is a ranking order that prioritise waste handling options relative to their environmental impact, starting at prevention, preparing for reuse, recycling of materials, recovery of energy, and lastly disposal as the least favoured option (fig 2.1). The main purpose of the directive is to ensure that waste and waste handling do not harm the environment or endanger human health. However, implementation of waste management hierarchy into the waste directive constitutes a shift within policy making, because the general idea behind the waste hierarchy affects the way waste is perceived from a previous perception of waste as a problem to the perception of waste as resource (Hultman & Corvellec 2012). In other words, the aim of the waste hierarchy is to encourage member states to "reintroduce as much material as possible into production processes"(Hultman & Corvellec 2012, p.2413)

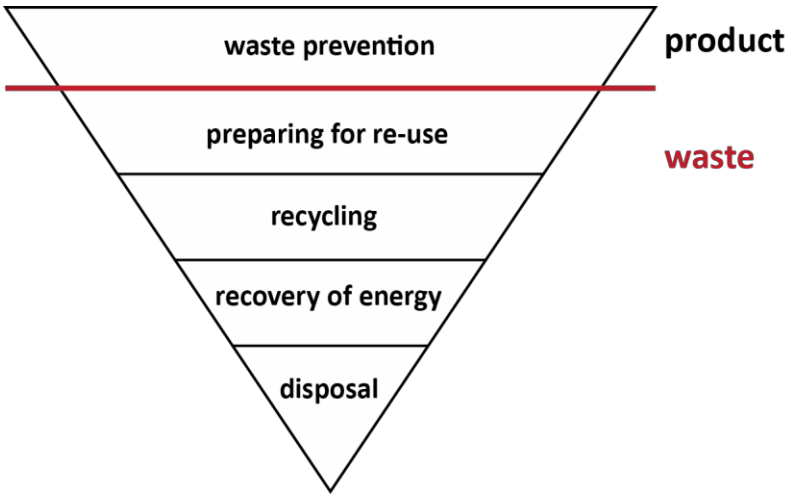

Figure 2.1 Waste management hierarchy (EC 2008b)

The incentives embedded into waste directive to achieve the aims of the waste hierarchy are based on the general principle of "polluter pays" (EC 2008a, p.3) and formulation of the *end-of-waste status* (EC 2008a, p.11). The *End of waste status* sets the legal binding criterions, which describe when waste ceases to be waste and becomes a secondary raw material. In the waste directive the definition of waste is simply "any substance or object which the holder discards or intends or is required to discard"(EC 2008a, p.9). To obtain the status as resource it requires that waste has gone through recovery and recycling operations. Furthermore, the substance must be suitable for a specific purpose, and fulfil technical requirements set by existing legislation. But equally important is that the waste material must not as secondary resource imposes adverse environmental and human health impacts. According to EU waste legislation this entails that an industrial produced by-product is a material, which can be used as resource in other industrial sectors without any further processing, whereas a waste material only can change status from waste to resource if it has undergone recovery and recycling preparations steps.

2.2 Sewage sludge ash as waste

This section gives a short description of sewage sludge ash (SSA) as waste and its potential use as resource. The specific SSA in focus derives from municipal wastewater treatment systems where incineration of the sewage sludge is applied. Sewage sludge is the solids, which during the wastewater treatment processes are separated from the liquids before the treated water is returned to the recipient water body (Fytili & Zabaniotou 2008). The sewage sludge is dewatered to increase the calorific value of the sludge and incinerated at temperatures around 800-900˚. SSA is the particulate inorganic remaining residue, which is captured in the flue gas cleaning system. The choice of waste handling option – incineration of the sludge, entails that sludge and SSA are labelled as waste. Consequently, in most cases, SSA is disposed at landfills and resources are lost. In Denmark however, SSA is deposited in special landfills without other types of waste, meaning that the phosphorous resource can be recovered, when proper techniques are developed.

Sewage sludge has a relatively high content of nitrogen, phosphorous and potassium, which are all nutrients essential for crops growth. Application of sewage sludge in agriculture is therefore considered as best practice if concerns about accumulation of heavy metals, organic pollutants in soils, and the spread of pathogens had not limited its general application as fertilizer and soil conditioner of agricultural land (Fytili & Zabaniotou 2008; Donatello & Cheeseman 2013; Reijnders 2014). Thus, aside from being a method to handle large quantities of sludge, incineration of sludge is also a way to deal with potential environmental and health risks which sludge represents. Overall advantages of incinerating sewage sludge, summed up by Fytili & Zabaniotou (2008), comprise: volume reduction, thermal destruction of toxic organic compounds, calorific values equal to that of brown coal and minimisation of odour generation. Nevertheless, these advantages do not change the fact that a main disadvantage is loss of fertilizer value.

2.3 Sewage sludge ash as resource

SSA has extensively been studied for its application in production of construction materials and components such as bricks, tiles and pavers (Donatello & Cheeseman 2013). The majority of studies have focused on the possibilities to utilise SSA as supplementary cementitious material (SCM) in blended cement. A major issue in the research on use of SSA as SCM is concerning the pozzolanic reactivity of SSA. A pozzolane is a finely divided siliceous and aluminous material, which in itself does not possess any cementing property; however it reacts chemically in the presence of moisture with calcium hydroxide to form cementing compounds (Mehta et al. 2014). The major elements of SSA are Si, Al, Ca, Fe and P, which in crystalline form constitute the minerals: quartz (SiO_2), whitelockite ($Ca_3(PO_4)_2$), and hematite (Fe_20_3) (Donatello & Cheeseman 2013). Overall, due to the proportional content of SiO_2, Al_2O_3 and CaO, SSA is within the spectra of latent pozzolanic materials (Lynn et al. (2015), though the content of SiO_2 and Al_2O_3 are significantly lower than other known pozzolanic materials such as coal fly ash (Cyr et al. 2007). Despite the similarities in regards to the constituents of pozzolanic materials like coal fly ash and blast furnace slag, SSA differs from these residues and other by-products in several ways. Coal fly ashes for instance consists of

large portions of amorphous and crystalline aluminosilicate phases, which are decisive for the reactivity of the material (Donatello & Cheeseman 2013; Mehta et al. 2014). Furthermore, it is combusted at much higher temperatures, which entails that glassy spherical particles are formed. The spherical particles influence the requirements of water, the workability, and the rate of strength of the concrete (Mehta et al. 2014). As the water to cement ratio (W/C) in a mix is the single most important parameter for the strength development of the concrete, coal fly ash can be used to decrease the amount of water, and at the same time increase the strength of the hardened concrete without affecting the workability of the fresh concrete (Mehta et al. 2014).

Research findings of conducted studies have in general shown that compressive strength and workability decrease when SSA is partially replacing cement in mortar (Monzó et al. 1996; Pan et al. 2003; Cyr et al. 2007; Garcés et al. 2008; Donatello et al. 2010a; Chen et al. 2013). SSA consists of coarse, angular and porous particles. Studies by Pan et al. (2003) and Donatello et al. (2010a) have discussed the impact of the morphology of SSA particles on the workability and the compressive strength of mortar by investigating the influence of grinded SSA on the performance of mortar. These two studies found that SSA initially has a high specific surface area which, however, did not increase proportionally to a decrease of the particle sizes when the SSA was grinded to obtain finer particles. The high specific surface area was found to be due to a porous structure of the SSA particles characterised by having many open pores. However, when these porous particles were grinded the morphology of the SSA altered from being coarse and porous to fine and less porous, and this had a positive effect on the workability and compressive strength development. It is generally accepted that the fineness of SCM is of importance for the early hydration process. This is because fine particles provide extra space and nucleation sites for the reacting compounds to form hydration products (Lothenbach et al. 2011). The explanation given for the increase of the compressive strength and the workability in the studies by Pan et al. (2003) and Donatello et al. (2010a) were similar but not quite the same. Pan et al (2003) suggested that the pozzolanic reaction only occurred on the outer surface as open pores of the unmilled SSA were blocked. Opposite Pan et al (2003) Donatello et al. (2010a) suggested that the open pores trapped the water and lowered the water, which consequently affected the hydration process of the reacting compound in the system. So even though the content of relevant siliceous and aluminous

compounds are not at the levels of known pozzolanic materials (Cyr et al. 2007), and different methods to assess the reactivity of SSA also have provided opposite results (Donatello et al. 2010c), the basic properties of mortar; workability and compressive strength are comparable to ordinary mortar when SSA is grinded before it is used as SCM. Grinding residue for qualifying the residue to be used as an SCM is not unusual. For instance blast furnace slag needs always to be grinded in order to react with the compounds of cement (Mehta et al. 2014).

Initially incentives to utilise SSA as resource in concrete production were primarily framed as an option to solve a waste problem (Tay, 1987; Bhatty & Reid, 1989). However, this perspective is slowly changing, and SSA is referred to as a secondary and useful material for production of blended cement and concrete (Donatello & Cheeseman 2013; Lynn et al. 2015). However, when SSA is considered as resource, the main resource is the content of phosphorous in the SSA. The concentration of P_2O_5 in SSA is reported between 10 -25 wt% (Donatello & Cheeseman 2013). Phosphorus pentoxide (P_2O_5) is the commonly reported constituent of the phosphate rock. The economic grade of phosphate rock varies from 25% to 37% P_2O_5 (Gupta et al. 2014). This concentration range corresponds to 11-16 wt% Phosphorous. Since the content of P_2O_5 in SSA is comparable to low grade phosphate rock (Donatello et al 2010b), SSA is a valuable resource of Phosphorous.

In 2013 a new national strategy *"Denmark without waste"* was formulated with the overriding purpose of preventing the loss of resources through utilisation of the resources available in waste (Danish Government 2013). The strategy was the legal response to the targets of the European waste directive defined by the waste management principles of the waste hierarchy. In the strategy aims for better nutrients exploitation was set. The ambition stated was that Denmark should recycle 80% of phosphorous from sewage sludge by 2018 e.g by recycling phosphorous in sewage sludge ash.

However, commercially viable large scale methods to extract phosphorous from SSA have not been fully developed, but primarily two groups of methods are under development: thermochemical and chemical extraction (Donatello & Cheeseman 2013). Currently, only one study by Donatello et al. (2010a) has tested SSA as partial cement replacement in mortar after phosphorous has been extracted. In the study sulfuric acid

was used as extraction agent. The effects of the treated SSA on the pozzolanic activity were evaluated by documenting the compressive strength development of mortars in which 20 wt% of cement was replaced by treated SSA. The results of the study showed that acid washed SSA had a negative effect on compressive strength as it decreased in comparison to the compressive strength of ordinary mortar and mortar with milled SSA.

In the present research two chemical extraction methods were used to recover the phosphorous from the SSA for recycling purposes as fertilizer. One method used hydrochloric acid to leach phosphorus from the SSA (Ottosen et al. 2013) whereas the other method used an electric current to acidify the SSA and hereby mobilise the phosphorous from the solid phase into a suspension (Ottosen et al. 2014).

3. RESEARCH QUESTION

In the framing of the present research, the findings of a previous project Biocrete (2008) was important. This project was a Danish demonstration project about SSA utilisation in concrete production. In the project it was reported that concrete significantly changed colour when increasing amounts of SSA were incorporated into the mix design. The transformation of colour was found as an obstacle, because the reddish colour differed from the usual grey colour of concrete. Thus, even though concrete with SSA met the technical requirements set for the actual concrete, the colour was seen as a limitation for its general application, unless the colour could intentionally be used for aesthetical purposes.

> *"Bio ash [SSA] concrete has a reddish colour especially when using iron bio ash. The colour is distinguishable from the ordinary grey concrete, and this might be a problem if the bio ash concrete is to be used for visible structures."*(Biocrete 2008, p.5)

Aim of the present research was to unfold aesthetical and technical potentials and constraints of SSA in concrete by taking into account the fact that SSA is a valuable source for phosphorus. The overall research question posed was:

> *How does SSA influence the performance of mortar aesthetically and technically when phosphorous is recovered from the SSA prior to use of the SSA as resource for production of cement based materials?*

In order to be able to answer the first question a second question was posed. This question defined the experimental frame of a material survey in which the aesthetical and technical potentials and constrains were investigated simultaneously by including colour as a parameter alongside with the most important basic properties relevant for the performance of concrete with SSA.

> *How do untreated, milled and phosphorous extracted SSA influence basic mortar properties such as: colour, strength, setting time and workability of mortar when 20 Wt % of cement is replaced by the different types of processed SSA?*

4. METHODS

The objective of the experimental work was to unfold the technical and aesthetical potentials of concrete with SSA. This was done by showing how basic properties evolved when the used SSA was processed by different methods prior to being incorporated into the mortar as partial cement replacement. Mortar was used instead of concrete as test material because mortar normally is used in the studies on SSA utilisation. The SSA was processed by different treatment methods which included: milling, acid washing and/or an electro dialytic treatment. The two latter are treatments methods which were used for the purpose of extracting the phosphorous in the SSA.

The experimental procedures used to determine mortar properties such as compressive strength, setting and workability were all valid international standards, as it enables results from one study to be compared with similar studies on SSA utilisation. The performed physical and chemical analyses of the test materials were also following international standards when possible. The use of standards as to document and determine the characteristics of a material are normally applied in a technical scientific context of engineering.

The visual transformation of mortar, how the mortar responded to parametrical changes of the SSA, was unfolded trough hands on experiments using the principals of paper cutting to produce rough and smooth surface of the mortars. Concrete is a receptive and versatile material. It can be rough and smooth, it has sensitiveness towards any imprints of the formwork; all depended on the materials used for the formwork and the accuracy of the work done. The contrasting textural qualities, the roughness and smoothness, its crude appearance and delicacy of imprints are all qualities, which are essential tools for an architect to express the architectural intentions of a building.

> *"most buildings consist of a combination of hard and soft, light and heavy, taut and slack, and many kinds of surfaces. There are all elements of architecture, some of the things the architect can call into play. And to experience architecture, you must be aware of all of these elements"*(Rasmussen 1962, p.29)

The paper cuttings were used as stencil in the mould to produce rough and smooth surfaces for the purpose of enhancing the colour experience through the contrasting textural qualities of mortar. The objective of these experiments was to provide a physical output that would exhibit the qualities of the mortars and make the potentials of SSA as resource in mortar perceptible by the senses useful for an aesthetical interpretation of the material in architecture. The experimental approach to unfold the aesthetical qualities of the transformed material is a design method normally for practitioners of ceramic design(Hansen 2010).

The combination of methods was chosen for the purpose of providing material relevant for different academic disciplines of Engineering and Architecture for a discussion on environmental, structural, and aesthetical potentials and constraints related to utilising SSA as resource.

4.1 Practice based research

The methods applied in the experimental work originating from the different disciplines of design and engineering were unified within the frame of a practice based research in design and art, described by Biggs in “Learning from Experience: approaches to the experiential component of practice based research” (2004). Biggs states that research is not practice based only for having a practical element or some consequence in experience, because “there are very few areas in which pure research is so disassociated from realm of practice and experience that it could not find any application”(Biggs 2004, p.2). It is more precisely the experiential component of the research and modes to communicate the experiential content. Biggs argues that experiential content cannot always be communicated effectively in a linguistic form perceptible to others. It depends on the context and therefore also audience, to whom the research is intended. Since knowledge production is the aim of research, modes to communicate the experiential content of the practice based research is important to define. The research which Biggs has in mind is “ investigations in which aesthetical judgements are made in relation to sensory object”(Biggs 2004, p.2). Biggs argues the experimentation in art and design arises through “realm of the experience rather than in the realm of

cognition"(Biggs 2004, p.3), and therefore, practice is not only an integral part of communication of outcomes, but also an integral part of the process of research in the field of art and design.

Even though the present research is aiming at reaching audiences of the different disciplines of architecture and engineering, the investigation of the research is directed by a design practice in which aesthetical interpretations of the materials are in focus. The pitfall of practice based research dealing with aesthetical judgements is that personal feelings -dislike or likes, cannot be the core of research. However, as the Danish architect Steen Eiler Rasmussen writes in his book *Experiencing Architecture* (1962) feelings cannot be excluded if one wish to pick up what is communicated through art "External features become a means of communicating feelings and moods from one person to another"(Rasmussen 1962, p.32). This statement given by Rasmussen's resembles the points of Biggs. However, as Biggs explains, the experiential feelings can't be the aim of research as these are personal. But as experiential content is represented by experiential feelings, experiential feelings can be the mean as to which the experiential content can be identified and perceived by others.

In design, artefacts may represent experiential content of the research, which cannot be effectively communicated linguistically to the audience for which the research is intended. The artefact is relevant when it gives answers to the research questions and supports the discussion on the subject in focus (Hansen 2010). In this present research the experiential component is related to the aesthetical potentials of concrete when SSA is used as supplementary cementitious material. To investigate the aesthetical potentials it necessitates an outcome that exhibits aesthetical potentials of the material so that they can be experienced. Investigations initiated were based on the experience from a previous study (Biocrete 2008), where it was found that the colour changed when SSA was used as resource in concrete. Variations in colours prompted by the introduction of secondary resources such as SSA into the mix design of concrete may challenge its general application in construction (Biocrete 2008). In a design context colour as well as the structural performance of building materials are essential material characteristics for an aesthetical interpretation of material in the build environment. Thus, the influence of SSA on the colour was chosen as the focus for an investigation of the aesthetical potentials of concrete with SSA. Therefor the aim of the present research was to unfold the

potentials by including colour as parameter to see how the SSA was influencing on the colour of the mortar alongside the basic properties: Compressive strength, setting time and workability.

5. EXPERIMENTAL WORK

The experimental work can be divided into three main studies:

1. Colour as an obstacle or potential – The influence of milled SSA on basic properties in mortar
2. Acid washed SSA in mortar
3. Electrodialytically treated SSA in mortar

Details of the three studies are presented in sections 5.1-5.3 and section 5.4 discusses the studies on an overall basis. In the first study, which was reported in two papers: *The colour potentials of SSA-containing mortar* and *Utilisation of Sewage sludge ash in mortar- the effect of milling on the compressive strength, workability and colour*, the experimental frame of the following two studies was clarified. Decisions were made about the SSA used in the experimental work, percentages for which cement was replaced by SSA; the constituents used for mortar production and treatments methods of the SSA. Two batches of an iron rich SSA (SSA1 and SSA2) provided by the wastewater company BIOFOS at their facilities in Avedøre, Copenhagen, Denmark were investigated. The SSA's was tested in mortar instead of concrete, which is common for research studies in this area. The main difference between mortar and concrete is the coarseness of the aggregates in the two materials. For mortar the aggregates ranges between 0- 4 mm whereas for concrete aggregates goes beyond 4 mm (Dam et al. 2008) The parameters decided to be included in the experimental frame were: compressive strength, workability, setting time and colour. These properties are basic properties, which have significance for the person working with the material as well as the scientist examining the material. Finally, a method was developed for the purpose of making diverse textural qualities of rough and smooth surfaces on the mortar sample.

In the two papers supporting study 2 and 3: *Technical, aesthetical and environmental potentials and constrains of utilizing acid washed sewage sludge ash as partial cement replacement in mortar* and *Utilisation of electrodialytically treated sewage sludge ash in mortar* two different types of phosphorous extracted SSA were tested as partial cement replacement by using the same experimental frame as described above.

5.1 Colour as an obstacle or potential - The influence of milled SSA on basic properties of mortar

The first experiments conducted in this research project surprisingly contradicted the general assumption that SSA influences and changes the colour of concrete from ordinary grey to a reddish colour (section 5.1.1).The results showed that the colour of ordinary mortar did not change significantly even when 10 - 20 *Wt* % of cement was replaced with SSA. What these experiments did show was that the colour induced by the SSA was conditioned by the grain size of the SSA and by the amount of SSA incorporated into the mix design. In two studies by Pan et al. (2003) and Donatello et al. (2010a) the use of milled SSA as partial cement replacement was tested. The results of the studies of Pan et al. (2003) and Donatello et al. (2010a) showed that the compressive strength and the workability increase when SSA is milled. The main reason was suggested to be due to trapped water in open pores of the porous particles of unmilled SSA, which adversely affected the hydration process between reacting cement compounds in the system (Donatello et al. 2010a). In the present study it was confirmed that the compressive strength and workability were increasing when the SSA was milled (section 5.1.2). However, the study also showed that the colour evolved from a grey tone to a slight reddish colour when the SSA was milled to obtain finer particles. Besides from the Danish project *Biocrete,* in which the colour of concrete with SSA was mentioned, colour as parameter has not been the focus of research up until now.

5.1.1 The Colour Potentials of SSA-containing Mortar

5.1.2 Utilization of Sewage Sludge Ash in Mortar - The Effect of Milling on Compressive Strength, Workability, and Colour

(Kappel, A., Ottosen, L.M. & Kirkelund, G.M.; 2017. Colour, compressive strength and workability of mortars with an iron rich sewage sludge ash. *Construction and Building Materials,* 157, pp. 1119-1205)

Figure 5.1Mortar samples with different percentage of SSA and milled SSA

5.1.1 THE COLOUR POTENTIALS OF SSA-CONTAINING MORTAR

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Abstract

This paper reports an experimental study of aesthetical qualities of mortar containing sewage sludge ash (SSA). SSA is the residue produced at water treatment plants where incineration of the sludge is applied in order to decrease volume and to prevent pathogens from spreading. Today SSA is with a few exceptions landfilled and thus, wasted.

The purpose of the experiments was to examine the influence of SSA and how it affected the colour of mortar samples. SSA was ground in 6 different intervals and added to mortar mixes by replacing 20% of the cement. An additional focus was to examine the possibilities to accentuate the colours of the hardened mortar by using paper cuttings in the production of the samples. The result of the experiments showed that a colour scale can be developed from ground SSA, and that paper may have the potential of providing divers textural qualities when it is used in combination with other form materials.

Keywords: Sewage sludge ash, colour potentials, mortar, textures.

1 Introduction

The cement industry is often singled out to be a considerable contributor to climate changes. Currently, cement production is estimated to be responsible for 5 - 8% of the total global emission of CO_2(Scrivener & Kirkpatrick 2008).

In the fifth assessment report by The Intergovernmental Panel on Climate Change (IPCC, 2014) “resource use efficiency” (Fischedick M., J & al. pp.59, 2014) is identified as essential but also one of several strategies to mitigate climate change. As part of this political agenda “Waste as resource” is also promoted in the waste hierarchy, as in the latest Waste Framework directive (2008/98/EC) of the European Union. The waste hierarchy, ranks waste handling options from most to less favoured in the order: prevention > minimization > reuse > energy recovery > disposal. The purpose of such a priority order is to strengthen resource use efficiency by regulating behaviour explicitly through the principle of “polluter pays”. Thus, scientifically and politically it is identified that mitigation of climate change necessitates a transformation of the way the available resources are governed. This also includes the resources that eventually end up on a landfill, such as SSA. To obtain a sustainable cement production in the future there are two main challenges: to reduce the CO_2 emission and increase the resource use efficiency. Thus, the advantage of replacing cement with SSA seems advantageous.

Several studies, (e.g. review by Cyr, Coutand & Clastres 2007; Donatello & Cheeseman 2013), have investigated the possibilities to utilize SSA as a supplementary cementitious material (SCM) with the potential of lowering the environmental impact of the cement production. The focus of the previously conducted research has mainly been on the chemical, mechanical properties and environmental consequences attached to the use of SSA in cement based materials (Cyr, Coutand & Clastres 2007; Chen & al. 2013; Donatello, Tyrer & Cheeseman 2010). One question which has sought to be answered is whether SSA possesses pozzolanic properties. In some studies SSA is compared to other by-products that possess pozzolanic properties but also advantageous characteristics such as spherical particles of coal fly ash . Generally, research has found that the compressive strength decreases when SSA partly replaces cement. The porous and coarse particles of SSA raise the water demand in the mix, and as such, SSA is not comparable to by- products with more obvious properties.

SSA also varies in accordance to parameters such as the level of industrial activity in catchment area, seasons and the processes applied at water treatment plant (Donatello & Cheeseman 2013). However

the process of grinding SSA has shown to improve the compressive strength of SSA - containing mortar (Donatello & al. 2010).

Some SSA has a distinct red colour due to chemical precipitation of phosphorus in wastewater treatment plants by iron. If cement is replaced by such SSA it can affect the colour of concrete which may challenge the traditional comprehension of concrete. Thus, to unfold the potential of utilizing SSA as SCM further, this study concentrated on the aesthetical qualities of using ground SSA in mortar. Thus, the aim of this study was to examine the colour development of hardened mortar samples when ground SSA was added to the mix by partly replacing the cement.

2 Experimental framework

This study included hands-on experiments for an investigation of: 1) the effect ground SSA had on the colour of the mortar samples and 2) the possibilities to use simple paper cuttings as a method to provide different textural qualities- rough and smooth surfaces.

Within the entire experimental study 50 samples were produced with varying percentage of cement replacement ranging from 10 to 50 % by weight. The SSA was also ground to obtain increasing fineness and larger specific surfaces areas of the SSA particles. The colour scale which was produced consisted of seven samples altogether; one mortar sample contained no SSA (reference) whereas the other 6 samples had 20 % cement by weight replaced by SSA grinded in the six different time intervals 0-10 min.

The samples originated from several separated experiments in which essential parameters were investigated: cement replacement percentage, time interval of the grinding procedure, and form materials. The focus was to detect the influence each parameter had on the colour of SSA containing mortar.

2.1 Materials

An iron-rich SSA was collected from Avedøre Spildevandscenter (AVE), BIOFOS in Denmark. The SSA was taken directly from the process line and stored in plastic containers at room temperature before use. Due to the high containment of Fe the SSA had a characteristically red oxide colour. A coarsely-grained sand, sea-sand 0-4mm, and a Portland cement labelled CEM II/A-LL 52.5R was used for the mortar production. This particular Portland cement used in the experiment had a content of 20 % of limestone filler.

2.2 Grinding process

The SSA was dried at 50 °C for 24 h before it was dry-milled for 6 different durations: 0 sec, 10 sec, 30 sec, 3min, 6 min, and 10 min. A vibratory cup mill (FRITSCH - pulverisette 9) was used for the milling.

2.3 Mortar and sample preparation

The basic recipe which was used for the mortar samples was 75 % sand, 25 % binder and a water/binder ratio of 0.5. The mortar was prepared in a small mixer with the capacity of 5 liters. Binder; either cement or cement and SSA, was placed in the bowl, and immediately after the water was added, the mixer was switched on for 30 sec at low speed. The sand was added during the next 30 sec, and then the mixer was switched to high speed and the mixing continued for another 30 sec. The mixer was stopped and the paste adhering to the inside of the bowl was within the next 30 sec removed by a scraper. After 60 sec of rest, the stirring process proceeded and the paste was stirred at high speed for another 60 sec.

The compaction procedure was executed by a vibrating table at a frequency of 53 Hz. The mortar was placed in the mould within the first 30 sec and the mortar was vibrated for another 90 sec. The mortar samples were sealed in plastic for 24 hours, unsealed and stored at room temperature.

The paper cuttings used to generate rough and smooth surfaces of the hardened mortar was created by cutting a circular shape out of the lining paper using a circle cutter. The paper was moistened by placing it under running water for a few seconds Fig. 1. Before the frame was mounted, the paper cutting was placed at the base of the mould and evened out with the means of a wall paper brush Fig. 2. The samples were casted in moulds made from film faced ply wood. The dimensions of the moulds were either 100x100x30mm or 200x200x30mm. For the colour scale a steel mould was used. The samples measured 80x40x40mm.

Fig. 1. The paper was moistened before it was **Fig. 2.** The wet paper glued to the base**.** placed on the base of the mould.

3 Results and discussion

The experiments of this study revealed that the colour of the SSA-containing mortar intensified as the time interval of the grinding process increased, Fig. 3. Each of the 6 steps within the time interval 0 – 10 min provided an additional colour tone and generated a colour scale consisting of mortar samples ranging from greyish to a more saturated red brown colour.

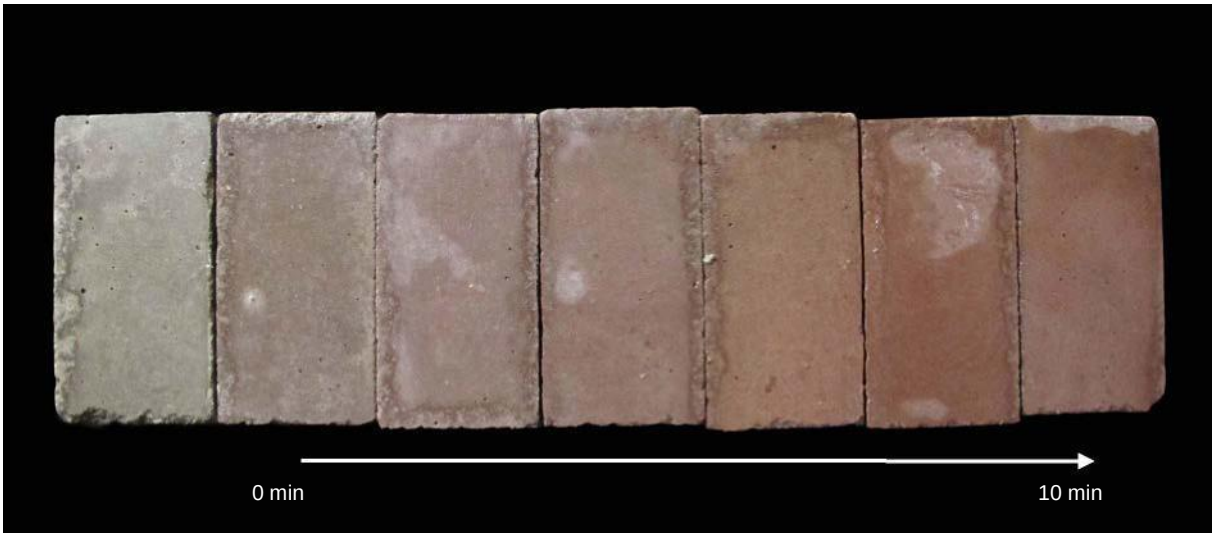

Fig. 3. Colour scale of moisturized mortar samples. The Grey colour of normal mortar gradually changes as the fineness of SSA particles increases. The first mortar sample to the left does not contain any SSA. The second sample contains un-treated SSA. Hereafter, the samples contain ground SSA of increasing fineness.

Additionally, the experiments revealed that the colour of mortar containing untreated SSA did not display a noticeable colour change particular when the samples had less than 20 % cement replacement. Fig.4.

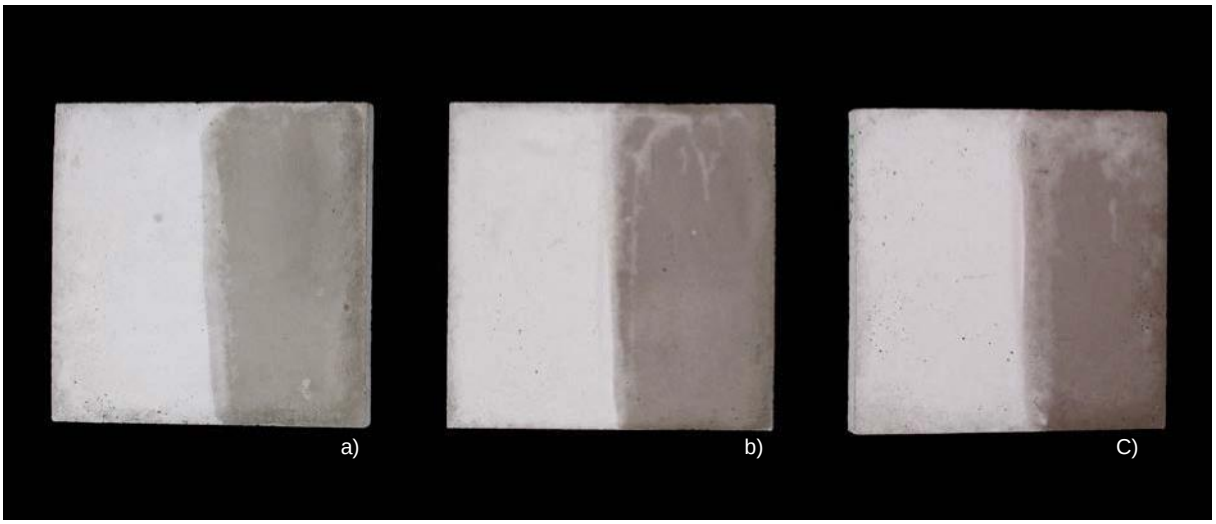

Fig. 4. a) sample –reference b) 10% cement replacement by un-treated SSA. C) 20% cement replacement by un-treated SSA. Half the tile was moistened .The Colour change was easier to see when the samples were wet.

Generally, increasing the SSA amount intensified the colour. Furthermore, it was found that the plain form materials -the film faced plywood and the lining paper generated diverse textural qualities in both rough and smooth surfaces. The rough and smooth surfaces highlighted the tones of the colour differently. Thus, the experiments displayed a possibility to influence the colour and to create circular imprints on the surface of the mortar samples Fig. 5.

However, the experiments also showed that the use of paper as form materials can cause technical challenges. In some cases the paper attached to the surface of the hardened mortar and it was not possible to remove it Fig. 6. Only by using a brush and running water did the paper detach. Consequently, the samples lost some of their vibrancy because the textural differences were blurred by this treatment. The reason why the lining paper sometimes was stuck to the surface was not identified and will need to be investigated further. Despite the fact that these form materials showed constrains in usage, the experiments exhibited a general idea of using absorbent and water repellent form materials combined to accentuate the colours of cement based materials which in this case was SSA-containing mortar.

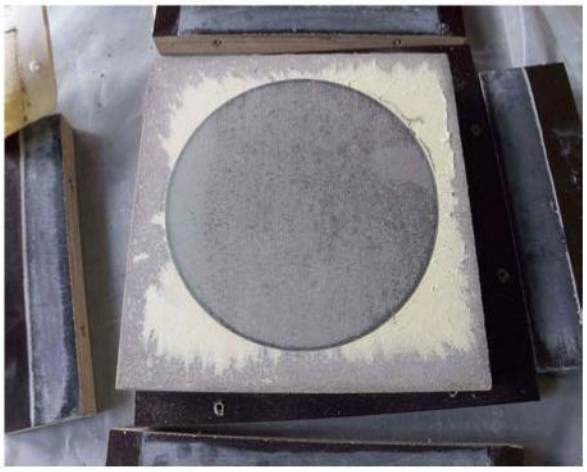

Fig. 5. Accentuation of colour displayed by the difference of rough and smooth surfaces. The circular parts are smooth and the surrounding areas are rough.

Fig. 6. Paper stuck to the hardened concrete tile.

The variability of SSA challenges it's suitability as SCM in cement based material. Nevertheless, Scrivener & Nonat 2011 advocate for the necessity to adjust future demands for cement by using locally available materials, and to develop on the basis of a scientific approach new SCM and cement types in order to produce sustainable cement based materials.

Empirical, initial testing of new materials such as SSA does not establish profound understandings of reactions on micro level and predictions of long term material performances at macro scale. Such testing will, however, often confront existing theoretical knowledge, pose new questions and unfold material properties, not perceived by a parametric model such as the aesthetical quality of a colour.

Even though the variability of SSA challenges its usage in cement based materials and application in construction, it also confronts the general idea and requirements for uniformity especially when thinking about concrete. For construction materials such as brick and wood, variation in colour and texture is in contrary, often desired and thrived for as aesthetical qualities that add value to the build environment. And although SSA containing concrete could be used at places where the colour is less important e. g in hidden structures there is also a possibility to incorporate variability into a design solution of a facade. As a good example can be mentioned Yardhouse designed by the London based architecture collective ASSEMBLE. The design solution for the facade exhibits how variation intentionally can be included by using coloured concrete tiles in an unusual scale for normal concrete facades Fig. 7. Thus, variation of cement based materials can be aesthetically unfolded trough rethinking scale and component. And as such, SSA shows potential as a secondary resource for colouring concrete, and if the aesthetical aspects such as colour are taken into account at an early stage, it could challenge a general idea that concrete is a grey, and in some views, a drab material.

Fig. 7. Yardhouse, 2014 by Assemble. The facade is made from concrete tiles. The colourful tiles is hand made on site. Photo:ASSEMBLE

4 Conclusions

This study revealed that SSA shows potential as a secondary resource for colouring concrete and a colour scale can be developed when different time intervals are applied to the process of grinding SSA. Additionally, the experiments displayed that the colour can further be accentuated by the use of simple form materials such as lining paper and ply wood. However, the usage of lining paper showed some technical challenges and is at present not applicable in large scale and optimisation needs to be investigated further.

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5.1.2 Utilization of sewage sludge ash in mortar - the effect of milling on compressive strength, workability, and colour

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Abstract

Sewage sludge ash (SSA) is the residue produced at wastewater treatment plants where incineration of sewage sludge is employed in order to decrease its volume. In Denmark, SSA is currently processed, with a few exceptions, as waste and is thus landfilled. This gives rise to environmental and economic problems for which solutions are urgently required.

This paper reports an experimental study of the colour, compressive strength and workability of mortar when cement is partly replaced by milled SSA. The SSA used in the present study had a high content of iron oxide which gave it a characteristically red colour. The SSA was dried and milled at 7 different time intervals ranging from 0-10 min and mortar samples with 20 % SSA replacing 20% cement were compared to samples containing no SSA.

The properties of the mortars increasingly improved with the duration of milling. The compressive strength of unmilled SSA was lower than the reference mortar, but when using SSA milled for more than 3 minutes, the same compressive strength was obtained for mortar with and without SSA. The workability of mortar containing SSA milled for between 3 - 10 minutes was comparable to the workability of ordinary mortar. At the same time, the colour intensified with the milling time, and a colour scale became available through this simple pre-treatment. The process of drying and milling are thus parameters which could qualify SSA as Supplementary Cementitious Material (SCM) used in blended cement.

Keywords: mortar, sewage sludge ash, colour, compressive strength, workability

1. Introduction

Negative environmental effects and over-exploitation of available resources, due to a growing human population, is one of the problems faced by the construction industry. Not only has the construction industry a high demand for materials, but 10% of the global emission of CO_2 is due to provision of construction materials of which cement alone is accountable for approximately 85 % [1]. The need for climate change mitigation has caused the cement industry to apply the concept of sustainability to its activities. Schneider et al.[2] analysed different strategies to reduce the emission of CO_2 associated with cement production. These strategies cover initiatives such as the use of alternative fuels and alternative materials in clinker production, kiln and grinding efficiency, carbon storage, production of cement with several main constituents, development of new clinker substitutes, and new types of binders and material concepts.

In the fifth assessment report by the Intergovernmental Panel on Climate Change [3] resource efficiency is recognized as a pathway to mitigate climate changes. Resource efficiency requires that the way available resources are governed is changed through their entire lifecycle. Thus, more political attention has been paid to the possibilities to utilize waste as resource. In the latest European Union Waste directive 2008/98/EC "waste as resource" is promoted by formulation of "end of waste criteria" which sets the legal framework that describes when waste cease to be waste and instead is qualified to obtain the status as secondary raw materials useful in industrial productions [4]. Industrial residues such as blast furnace slag, silica fume and coal fly as have for a long period of time been utilised for concrete production, and utilisation of waste products retrieved from other sectors are therefore not new within the concrete industry. This has led to conditions where 20 -70 % of cement [5] is replaceable with silico-aluminate materials that fills out the function as supplementary cementing material (SCM) in blended cement and such utilisation complies with the concept of resource efficiency. However, in order to achieve higher rates of cement substitution for the purpose of lowering the CO_2 emission due to clinker production, it is necessary to develop and use new SCM which also are locally available [6]. Aside from naturally occurring resources such as natural pozzolanes and activated clay, sewage sludge ash (SSA), a residue that derives from incinerating sewage sludge, could be such a local available resource suitable for SCM. Research has investigated the possibilities of utilizing SSA

not only as SCM in blended cement but in a wide range of building materials such as bricks, tiles, pavers, light aggregates but also for substitution for cement in concrete and mortar [7–9]. Results reported in literature on the compressive strength development, workability and setting time of mortar onconcrete containing SSA have however, shown that these properties are negatively affected when compared to the same properties of ordinary mortar or concrete. However, studies by Pan et al. [10] and Donatello et al. [11] (2010) have found that compressive strength development and workability can be improved when the SSA is milled to obtain finer particles.

So far studies conducted have mainly performed tests on SSA as SCM in mortar and concrete at laboratory scale. One exception was the Danish demonstration project *BioCrete* [12] where utilisation of SSA in concrete production was tested on a larger scale. In the project the milled SSA was replacing coal fly ash by 50 % as the pozzolanic activity of SSA was found too low to replace cement. However, due to a high content of Fe in the SSA the colour of the concrete changed from the normal grey to increasingly red tones [13]. The change of the colour was addressed as an obstacle as it was stated that the red colour restricted the application of the concrete mainly to be used for hidden structures if not intentionally used aesthetically. Thus, in a previous study by Kappel et al. [14] the change of colour in SSA-containing mortar was addressed as an aesthetical quality, which was unfolded by investigating how the colour evolved when the fineness of SSA increased. In the previous study initial tests revealed that the colour did not change significantly unless the SSA was milled to obtain finer particles and thus, it was found that the milling of an Fe rich SSA was a requirement for the red colour to evolve. The objective of the present study was to examine how SSA affected the compressive strength, workability and the colour of SSA-containing mortar. The three parameters were chosen as these basic material properties are seen as indicators for the applicability of using SSA as SCM in cement based materials.

2. Materials and methods

2.1. Materials

SSA was collected at the wastewater treatment plant Biofos in Copenhagen, Denmark (February, 2013). The SSA is incinerated in a fluidized bed combustor at about 850°C. The plant treats wastewater from 255.000 person equivalents (PE) with a subsequent ash production of app. 2500 tons annually. Phosphorous is removed from the wastewater by chemical precipitation with Fe. The resulting ash therefore has a characteristic red iron-oxide colour. The SSA was collected directly from the process line and stored in sealed plastic containers at room temperature. The SSA was both used as-received and milled, and these samples are named SSA and SSA_{Xmin}, respectively, where x is the duration of the milling.

For mortar preparation a Portland cement (CEM II/A-LL 52.5R) was used. This cement type has a content of less than 20% limestone filler. The sand used in the experiment was a natural sea sand 0-4mm with technical specification following DS/EN 12620 ([15] 2008) and DS 2426 [16] In this paper, the term “test material” covers SSA (as-received and milled), cement and test binders (cement and SSA).

2.2 Drying and milling procedures

The effect on the particle size distribution of milled SSA after drying at two different temperatures (50 °C or 105 °C, for 24 h) was investigated. The SSA was dried before the milling and compared to SSA which was dried after the milling, SSA as-receieved and cement. The milling duration was 30 sec and the particle size distribution was analysed by laser diffractometry. A vibratory cup mill (FRITSCH - pulverisette 9) was used for the milling. For the remaining part of the work, the procedure for drying and milling was: drying at 50 °C for 24 h before milling. Milled SSA samples from 6 different durations were produced: 0 sec, 10 sec, 30 sec, 3min, 6 min, and 10 min. Particle size distribution was measured for each fraction and they were compared to the particle size distribution of cement.

2.3 Analytical procedures

The concentrations of the trace elements Ni, Cr, Cu, Zn and Pb in the test samples were measured after the pre-treatment procedure described in DS/EN 259 [17]: 1.0 g material and 20.0 ml (1:1) HNO3 was digested at 200 kPa (120 °C) for 30 min. The digested suspension was filtered through 0.45 µm filter paper, and the filtrate analysed by ICP–OES (Induced coupled plasma – optical emission spectrometry). The water content of the test samples were measured as weight loss by drying at 105°C for 24 hours. The pH was measured by suspending 10.0 g of test material in 25 ml distilled water. After 1 h agitation pH was measured directly in the suspension. Loss on ignition (LoI) was determined as weight loss after 30 minutes at 950 ˚C. Solubility in water was evaluated by suspending 100 g test material in 500 ml distilled water. After agitation for 1 min and settling, the water was decanted and 500 ml new distilled water was added. This was repeated and the ash was washed three times. Finally the suspension was filtered, dried and weighed, and the solubility expressed as weight loss by this procedure. The buffering capacity of the test materials was determined by firstly preparing a suspension of the test material mixed in water (6.7 % w/v) secondly stirring the suspension for 30 min before pH was measured. Successive 10 ml of concentrated HCl were made every 30 min and pH was measured thereafter. This was repeated every 30 min until pH was below 2 [18]. Major oxide composition and Cl content in SSA and cement was found by X-ray fluorescence (XRF) on powder samples. Images of particle morphology were made using a scanning electron microscopy (SEM) of a small sample placed directly on carbon tape. The accelerating voltage of the SEM was 15 kV and it was equipped with a large field detector and x-ray cone. Particle size distribution of the test materials was determined by laser diffractometry.

2.4 Mortar preparation and compressive strength test

The mortar preparation followed the procedures as described in DS/EN 191-3+A3 [19] except for the sand, where the 0-2 mm sand prescribed was replaced by coarser sand with a grain size distribution between 2- 4

mm. This sand was chosen to have a coarser consistency, closer to that of concrete, but still manageable at laboratory scale.

In the experimental mortars 20 % by weight of the cement was replaced by SSA. This percentage was chosen to obtain results that would clearly show what effect milled SSA had on colour, compressive strength development and workability. The same percentage of cement replacement was used in two studies in which milled SSA was tested for pozzolanic activity [10], setting time and workability [9]. 20 % cement replacement can also be seen as an appropriate starting point for dealing with the environmental implications of cement production. Seven experimental mortars were produced, five with substitution of milled SSA, one with substitution of SSA as received ($2._{0sec}$) and one control sample without SSA ($1._{ref}$) No additional water was added to any of the test samples. A description of the different mortars is shown in Table 1. The mixing, casting procedures and the moulds used were as prescribed by DS/EN 191-3+A3 [19]. The mortar samples were removed from the moulds after 24 h, placed vertically in a water bath 20 °C and cured for 28 days. Each prismatic mould produced 3 specimens measuring 160mm x 40mm x 40mm which after curing were cut into 6 equal test samples measuring 80mm x 40mm x 40mm. For the determination of the compressive strength a Toni 3000 compression machine was used. The compressive strength test followed the prescription given in standard DS/EN 191-3+A3 [19] and was applied after 28 days. The seven different mortars listed in Table 1 each consisted of six identical test samples that were all tested.

Table 1 Recipe for reference and test mortars

sample	duration of milling	cement	SSA	sand	water
$1._{ref}$	÷	450 g	÷	1350 g	225 g
$2._{0sec}$	0 sec	360 g	90 g	1350 g	225 g
$3._{10sec}$	10 sec	360 g	90 g	1350 g	225 g
$4._{30sec}$	30 sec	360 g	90 g	1350 g	225 g
$5._{3min}$	3 min	360 g	90 g	1350 g	225 g
$6._{.6min}$	6 min	360 g	90 g	1350 g	225 g
$7._{10min}$	10 min	360 g	90 g	1350 g	225 g

A characterisation of test materials used in the experiments included SSA as received (SSA), cement, milled SSA (SSA_{10min}), and the two test binder consisting of 80% cement and 20 % SSA as received or milled. The test binders were named Binder_ 20%SSA and Binder _ 20%$SSA_{10min.}$

2.5 Workability

The flow value expresses the workability of mortar with un-treated and milled SSA. Preparation of mortars followed DS/EN 191-3+A3(DS 2009) and the tested mortars are those listed in Table 1. The flow value was determined according to DS/EN 1015-3 [20]. A truncated conical mould (50 mm high, internal diameter 100 mm at the bottom and 70 mm at the top) was uniformly filled with mortar. The mould was removed, and the mortar exposed to jolting by slowly raising the mould 2 cm vertically and dropping it, 15 times at a rate of one pr. second at a flow table. The mean diameter (d_{mean}) from two measurements of the subsequent mortar diameter in two directions at right angles was found. The procedure was repeated twice for each mixture. The flow value is defined as D_{mean} of second measurement and accepted, if D_{mean} differs less than 10 % between the two mixtures.

2.6 Colour samples

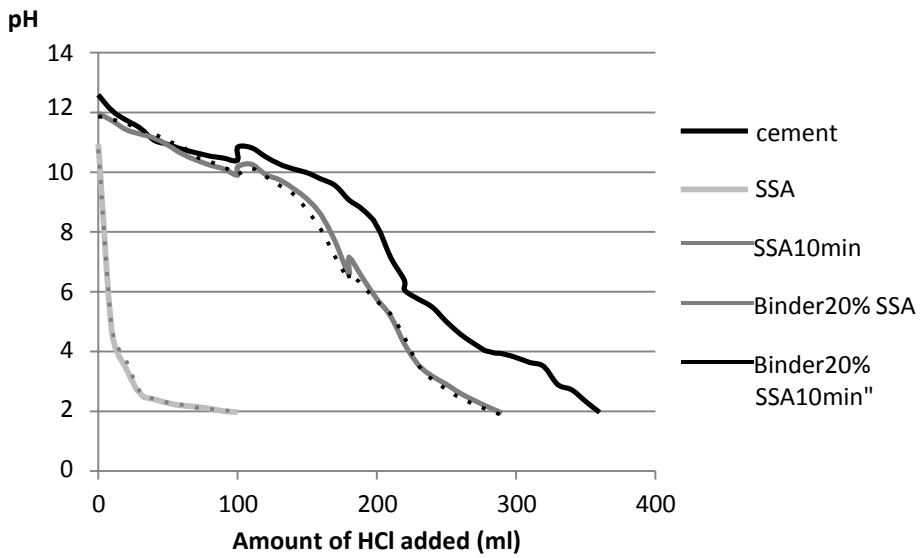
The seven mortars in Table1 were prepared for the production of samples for colour evaluation. The mixing followed the same procedures as for compressive strength testing. However, the moulds used were three compartment moulds made from film faced ply wood where each compartment had the internal dimensions 100x100x30mm. The mortar was uniformly distributed in the mould by means of a vibrator table, covered in plastic and kept in the wooden mould for 24 h. The samples were ejected and stored at room temperature without any exposer to daylight.

3. Results

3.1 Material characteristics

The characteristics of the test materials: SSA, SSA_{10min}, cement, Binder_20%SSA and Binder_20%SSA_{10min} are shown in Table 2. The results showed that all test materials were alkaline. However, the pH of SSA and SSA_{10min} were lower than the pH of cement and test binders, as these were pH 9.9 and 9.4 against pH 12.6 respectively. Thus the pH of the two test binders was the same as in the pure cement sample. This finding was supported by findings provided by the determination of the buffering capacity (Figure 1).The graphs monitoring the buffering capacity of cement displays a high resistance against acidification as the pH dropped slowly. Even though the buffer capacity of SSA and SSA_{10min} were significantly lower in comparison to cement, the buffer capacity of the two test binders showed to some extent equal resistance against acidification as for cement despite the fact that 20% of cement was replaced by SSA of lower pH and buffer capacity.

Figure 1 Buffer capacity of SSA, SSA10min, cement and test binders (Binder_20%SSA and Binder_20%SSA10min



The SSA had a water soluble fraction of about 1.5% per weight (Table 2). Determination of water solubility gave negative values for cement and the two test binders. The negative values represent an increase in mass

due to the hydration process. The values found display that the hydration process of the test binders was less reactive as these values were less negative than for cement.

The chemical analysis showed that the concentrations of trace elements Cu, Zn and Pb were significantly higher in the test binders than in cement due to the higher concentration levels in the SSA. The concentrations of Cr and Ni, on the other hand, were only slightly elevated in the test binders compared to cement.

Table 2 Characterisation of SSA, SSA10min, Cement and test binders (Binder_20%SSA and Binder_20%SSA10min)

	SSA	SSA_{10min}	cement	Binder_20%SSA	Binder_20%SSA_{10min}
water content %	0.63 ± 0.13	0.06 ± 0.10	0.28 ± 0.11	0.24 ± 0.09	0.47 ± 0.16
water solubility %	1.27	1.5	− 3.56	− 1.93	−2.01
pH	9.9 ± 0.00	9.4 ±0.00	12.6 ± 0.02	12.6 ± 0.01	12.6 ± 0.02
Loss on ignition (%)	1.35 ± 0.04	1.62 ± 0.08	7.04 ± 0.09	5.81 ± 0.05	5.72 ± 0.62
Major oxides (%)					
Al_2O_3	5.1	−	4.91	4.95*	−
CaO	23.8	−	65.7	57.5*	−
Fe_2O_3	15.7	−	5.43	7.48*	−
K_2O	1.57	−	0.81	0.96*	−
MgO	2.32	−	0.53	0.89*	−
MnO	0.09	−	0.04	0.05*	−
Na_2O	1.15	−	0.67	0.77*	−
P_2O_5	20.2	−	0.23	4.22*	−
SiO_2	17.1	−	20.1	19.5*	−
SO_3	2.02	−	4.74	4.2*	−
TiO_2	0.83	−	0.35	0.45*	−
Cl	0.01	−	0.1	0.08*	−
trace elements (mg/kg)					
Ni	57.5 ± 1.53	57.7 ± 4.29	27.0 ± 5.55	35.6 ± 1.15	35.0 ± 1.23
Cr	38.7 ± 0.76	43.6 ± 2.96	26.0 ± 4.85	30.7 ± 2.11	29.8 ± 1.64
Cu	688 ± 17.3	703 ± 54.9	67.5 ± 13.1	183 ± 8.12	183 ± 6.98
Zn	1930 ± 26.8	1960 ± 67.5	115 ± 22.0	415 ± 17.0	413 ± 17.2
Pb	144 ± 2.00	146 ± 7.65	21.6 ± 4.49	46.3 ± 1.56	45.9 ± 1.48

* calculated oxide content on basis of the detected content values of SSA and cement

The distribution of the major oxides for SSA was: CaO > P_2O_5 > SiO_2 > Fe_2O_3 > Al_2O_3 (Table 2). The content of P_2O_5 was 20 % and was at the same level as CaO (23.8 %) and Fe_2O_3 (17.5 %). When SSA and the content of four main constituents of cement: CaO, SiO_2, Fe_2O_3 and Al_2O_3, are compared, only the content of SiO_2 was at a comparable level in the SSA to the content found in cement. MgO and MnO were found to be

between 2- 4 times higher in SSA than the levels found in cement. Only the content of SO_3 was higher in cement than in SSA which was 2.02 % against 4.74 % for cement. The major oxides composition for Binder_20%SSA was calculated on basis of the measured compositions for the two parts SSA and cement (Table 2) and it had quite similar composition as cement. The concentration of P_2O_5 was however, much higher (4.2% against 0.2%) for Binder_20%SSA due to the high content in SSA. The complete lists of order in weight percentage of the major oxides in SSA, cement and Binder_20%SSA are:

SSA: $CaO>P_2O_5>SiO_2>Fe_2O_3>Al_2O_3>MgO>SO_3>K_2O>Na_2O>TiO_2>MnO>Cl$

Cement: $CaO>SiO_2>Fe_2O_3>Al_2O_3>SO_3>K_2O>Na_2O>MgO>TiO_2>P_2O_5>Cl>MnO$

Binder_20%SSA $CaO>SiO_2>Fe_2O_3>Al_2O_3>P_2O_5>SO_3>K_2O>MgO>Na_2O>TiO_2>Cl>MnO$

The results of the particle size distribution analysis seen in Figure 2 showed that finer particles were obtained if SSA was dried before milling regardless the applied temperature. Samples of SSA were dried either before (Bef) or after (Aft) milling at 50°C and 105°C. At 50 % of volume for $Aft_{50°C}$ the accumulated volume had increased by approximately 10 % in comparison with $Bef_{:50°C}$. Thus finer particles were obtained when the SSA was dried before the milling. The applied temperature did not affect the particles size distribution. Based on this result, the SSA was dried at 50°C before it was milled in order to obtain the smallest possible particle sizes in the remaining experiments.

Figure 2 Particle size distribution of cement, SSA as-received, and milled (30 Sec) SSA dried either before (Bef) or After (Aft) the milling

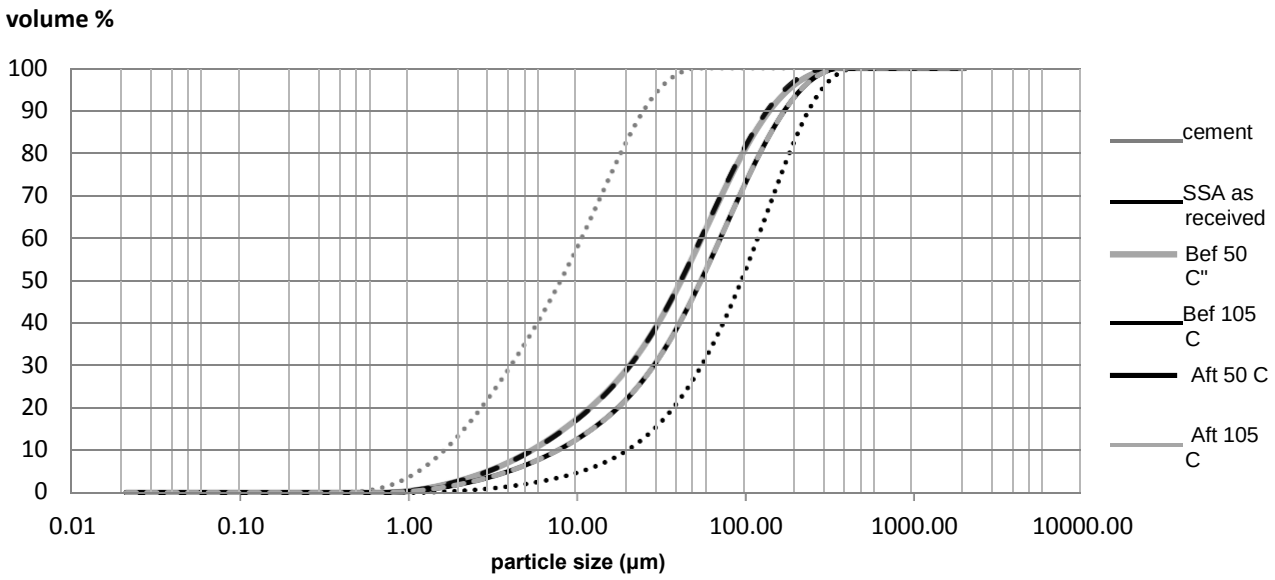
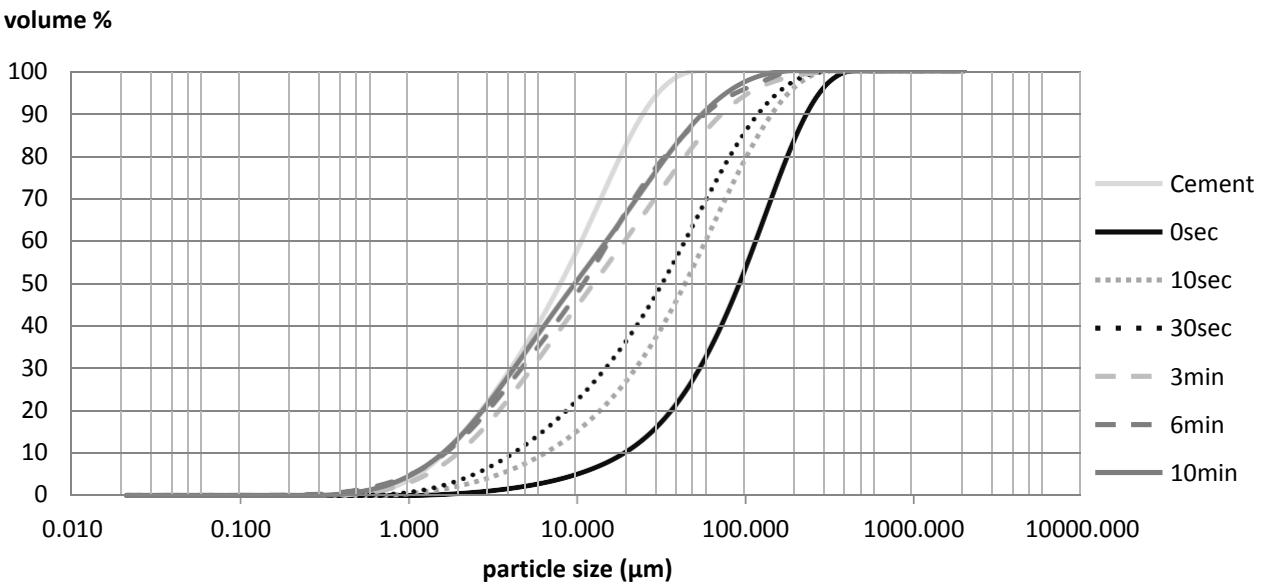


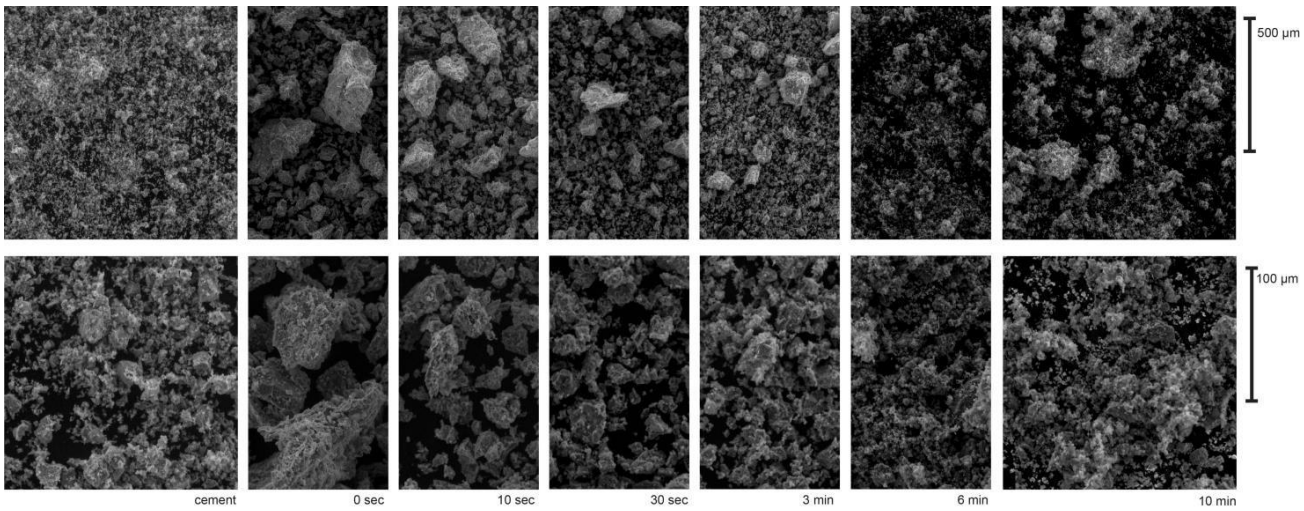
Figure 3 Particle size distribution of cement and SSA milled in interval between 0 sec and 10 min



The effect of the milling process for different durations was analysed by comparing the particle size distribution and morphology of the milled SSA with the particle size distribution and morphology of cement

(Figures 3 and 4). The effect of milling SSA can be seen in Figure 3. A comparison of the particle size distribution for the milled SSA shows that the slopes of the curves and the medium size particles (d_{50}) move closer to that of cement as the duration of milling increases. The increase in particle fineness is slower in the duration from 3 to 10 min (Figure 3). SEM images of the morphology of un-treated, milled SSA and cement (Figure 4) support the findings from Figure 3. The effect of the milling on the coarse particles of un-treated SSA, which were steadily crushed as the duration of the milling increases, were observed. As a result of the milling, the finely grounded ashes milled for 6-10 min (Figure 4) attained uniformity, which is equivalent to cement.

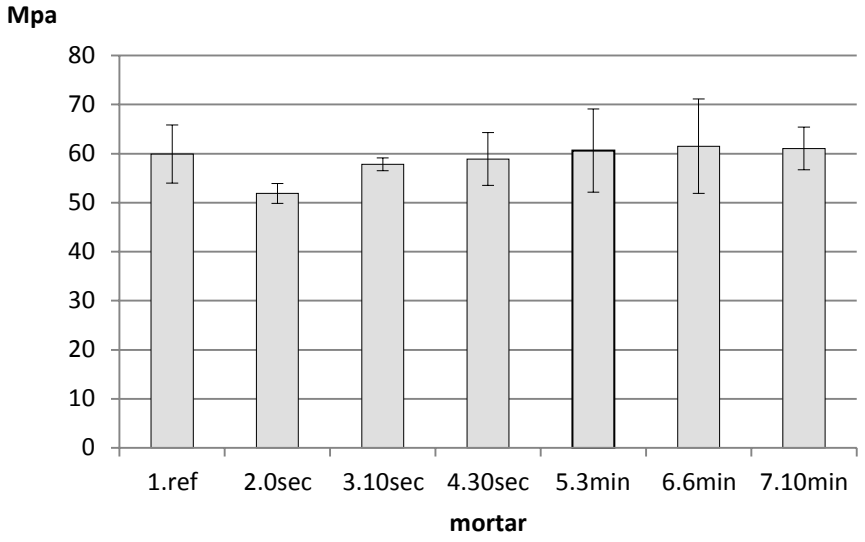
Figure 4 SEM images of cement and milled SSA in interval 0sec- 10min



3.2 Material properties: compressive strength, workability and colour

The results of the compressive strength test (Figure 5) showed a positive effect from milling the SSA. A decrease in compressive strength was found when 20 % of cement was replaced by untreated SSA. The measured compressive strength of the control ($1._{ref}$) was around 60 MPa and decreased by 13.4% to the level of 52 MPa ($2_{untreated}$) when cement was replaced by SSA as receieved. However, the compressive strength improved immediately when SSA had been milled, even for only 10 sec. The compressive strength for 3_{10sec} was approximately 58Mpa, a decrease of only 3.4% compared to the compressive strength of $1._{ref}$. Test mortars containing SSA milled for 3- 10 min achieved the same level as $1._{ref}$.

Figure 5 Compressive strength of reference mortar and test mortars after 28 days of curing at 20°C



The workability, evaluated by determining the flow value of test mortars, is seen in Figure 6. The particle size distribution of SSA was essential to the workability of the six test mortars. The flow value of $2._{0sec,}$ where 20 % cement was replaced by SSA as received, decreased by 35% in comparison to $1._{ref}$. As the milling duration increased, the flow values increased correspondingly. For sample $6_{6min,}$ the flow value was close to that of $1._{ref}$.

Figure 6 Flow value -Workability of control and test mortar

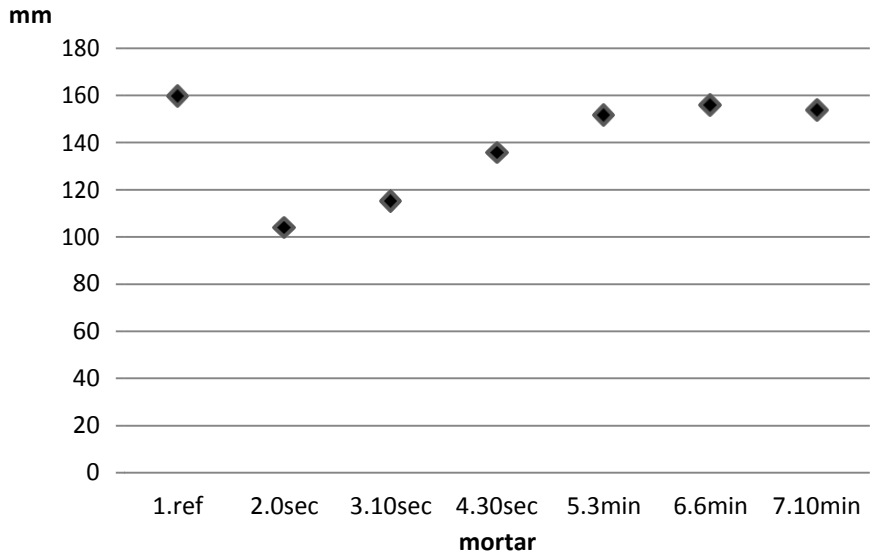


Figure 7 shows the colour samples. It shows that the colour of mortar containing milled SSA evolved simultaneously to an increased duration of the milling (Table 1). The images also display that the colour tone

of 2_{0sec} was comparable to the grey colour of $1._{ref}$ which had a grey colour with a slight red tint. This supports the findings in Kappel et al [14]). This study showed that a precondition for having a pronounced change of colour for mortar containing an iron rich SSA was to mill SSA into finer fractions. In Figure 8 the three samples: $2._{0sec}$, $3._{10sec}$ and $6._{6min}$ are displayed together with $1._{ref}$, and it illustrates that the colour progression of the six samples containing SSA can be ordered in a three step colour scale. In the colour scale each of the samples has a distinct colour different from the neighbouring sample. The remaining samples which are not included in the colour scale in Figure 8 have tones which are similar to the samples: $2._{0sec}$, $3._{10sec}$ and $6._{6min.}$

Figure 7 Colour samples of reference mortar, as received and milled SSA arranged in the following order. 1.ref – 7.10min

Figure 8 Colour samples 1.ref 2.0sec, 3.10sec and 6.6min

4. Discussion

The use of SSA as SCM in blended cement may not seem so obvious when you compare SSA to the use of other residues with more evident properties such as lubricant effect of coal fly ash particles or the high reactivity of silica fume. On the contrary result reported in literature have generally showed that properties of mortar such as the compressive strength and workability are impaired when SSA is used partly to replace the cement [7, 9 ,20–23]. The reason is the parameters which are important for the pozzolanic activity of SSA are not optimal in SSA. Firstly , the content of reactive silica and aluminous are generally lower for SSA than other known SCMs [7], and secondly, SSA are characterized by irregular, coarse and porous particles which affect the fluidity of the fresh mortar and lowers the available water for the hydration process in the system [9,10]. However, results on compressive strength tests and determination of the workability of the test mortars in this present study indicate that it is possible to obtain a material which is suitable as SCM by applying simple pre-treatments methods such as drying and milling.

Generally, the reaction rate of most SCMs is slower than the reaction of clinker phases, and the filler effect is main parameter contributing to formation of hydrations products at an early stage [24] . The fineness of the SCM is therefore important, as fine materials with large surfaces enhance nucleation sites and provide more space in the system for the clinker phases to form hydration products. The findings of the present study supports the findings of Donatello et al. [11] and Pan et al. [10] as the results produced in all three studies showed that the compressive strength improved when SSA was milled. Contrarily to the results obtained in the study of Donatello et al. [11], the time intervals in the present study did not result in particle size distributions that exceeded the fineness of cement. On the other hand the milling time applied did provide a material which could replace the cement by 20 % and at the same time obtain compressive strengths and flow values which were comparable and reached the level ofreference mortar. The results on the compressive strength development in the studies by Donatello et al. [11] and Pan et al. [10] reached to 94 % and 77 % of the reference mortar respectively.

Besides the chemical composition, the amount of reactive phases and the fineness of the particles; the composition of the interacting solution is equally important for the reactivity of pozzolane [24]. However, for the majority of studies the reactivity of SSA has not been discussed in relation to the interacting solution. Exceptions are two previous studies by Monzó et al. [21, 25] in which SSA was tested as partly cement replacement in mortar and tested in relation to four different types of cement. The results reported from the compressive strength test showed that the strength development was dependent on the cement used. Even though the results from the present study and the study of Donatello et al. [11] are not directly transferable for a comparison due to the differences in the cement, sand and SSA used, it may exemplify the relevance to include the role of the interacting solution to assess the pozzolanic activity since the compressive strength of 5_{3min}, 6_{6min} and 7_{10min} reached the compressive strengt of 1_{ref}. In order to broaden the discussion on SSA as secondary resource suitable as SCM, we consider it necessary to assess all the parameters brought into play collectively both the specific SSA and clinker phases present. To answer and understand how SSA interact with the clinker phases it may require as Scrivener & Nonat [6] suggest more advanced assessments methods as parametric modelling based on profound knowledge on thermodynamics of the compounds to determine the hydration products formed and thus be able to predict the long term performance of the cement based material produced.

Furthermore, colour and the colour change due to the SSA may have to be overcome before SSA will obtain the status as SCM. In the project Biocrete [12] colour was used as marker for the quantities to be used in order to avoid the colour of concrete to change, even though concrete with a reddish colour containing a higher amount of SSA met the technical requirements set for the concrete [26]. The colour samples produced in this study display that the colour changed from the normal grey to a reddish colour when the SSA was milled and increased when the fineness of the particles increased. If the motivation for utilizing SSA is to reduce the amount of the CO_2 intensive clinker by substitution of SSA, the colour of the concrete seems less important as a measure to control the substitution rate. In general however, colour does not play a major role in research on SSA utilisation, as the studies conducted do not refer to any colour change due to the SSA used. This could be due a disengagement with the subject as the colour is not important for the application [

[27]. However, exemplified by the Biocrete project, the colour change may be regarded as a limiting factor for a general application in concrete, and therefore we believe that the colour of SSA containing mortar and concrete is relevant to address to unfold the colour potential of milled SSA which intentionally can be used aesthetically and/or integrated in the design solution.

5. Conclusion

- Finer particles can be obtained if SSA is dried before milling regardless the applied temperature.
- The milling of the SSA improves the strength development and the workability of SSA containing mortar.
- The use of 20 % of SSA milled between 3- 10 min provided compressive strength and flow values that were comparable to the compressive strength and the flow value of ordinary mortar.
- The colour change of mortar is not significant unless the SSA is milled. However, mortar containing 20 % of SSA_{0sec} obtained a grey colour with a slightly red tint, which evolved as the duration of milling increased to the extent that mortar changed colour from light grey to a reddish colour for mortar containing $SSA_{6\text{-}10min}$.
- It is possible to obtain a material which may be suitable as supplementary cementitious material by applying these simple pre-treatments of SSA: drying and milling. However, the question of the reactivity of SSA and its long term performances may have to be settled before SSA can obtain the status as secondary resource suitable as SCM in blended cement.

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5.2 ***Acid washed SSA in mortar***

The experimental work of the second study was conducted as part of a collaboration project "*Genanvendelse af fosfor fra slamaske*" between the engineering consultant company Rambøll, University of Southern Denmark (SDU) and Technical University of Denmark (DTU). The project was supported by the Danish Environmental Protection Agency (EPA). The overall aim of this project was to further develop a wet chemical extraction method to recover phosphorous by using hydrochloric acid to extract the phosphorous from the SSA (Ottosen et al. 2013). This method was previously found to be an efficient method to solubilise the phosphorous and separate it from the solid residue. However one important challenge was identified, which was the impurity of the final phosphorous product due to high levels of heavy metals. Therefore, further development was required to optimize the crystallisation process to be able to form large calcium phosphate crystals having low levels of heavy metals.

At the same time, the present investigation of the residue left after acid extraction was included to examine whether it could be used as partial cement replacement in mortar. The task of the second study was therefore to investigate how the basic properties of mortar were affected by the acid washed SSA (section 5.2.1). The results of the study showed that mortar with acid washed SSA obtained a compressive strength which was comparable to ordinary mortar. Similar behaviour was seen for the workability of the fresh mortar which was less fluid. The workability improved, however, when the acid washed SSA was milled. Due to the acid washing of the SSA the colour of the mortar changed significantly from the ordinary grey to a red earth tone. But the colour did not evolve any further when milled acid washed SSA was used in the mortar.

5.2.1 Technical, Aesthetical and Environmental Potentials and Constraints of Utilizing Acid Washed Sewage Sludge Ash as Partial Cement Replacement in Mortar

5.2.1 Technical, aesthetical and environmental potentials and constraints of utilizing acid washed sewage sludge ash as partial cement replacement in mortar

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Abstract:

Phosphorous is an indispensable nutrient necessary for crops growth. Since the present sources for phosphorous are depleting, recirculation of phosphorous and the need to develop sufficient extraction methods are increasingly brought into focus at a political level. Currently, sewage sludge ash (SSA) is an untapped source for phosphorus which potentially could be retrieved by acid extraction. Over the years research has extensively studied possibilities to utilise SSA as substitute for cement in concrete and mortar, equal to other industrial residues like coal fly ash. However, only few studies have included the aspects of phosphorous recovery. The purpose of this study was to examine how basic material properties of mortar were affected when 20% of cement was replaced by treated SSA. To extract phosphorous the SSA was washed in HCl before it was milled into six different finenesses (time intervals from 0- 10 min). For comparison untreated SSA was milled into the same six fractions. The experimental framework covered a study of which the effect the treated and the untreated SSA had on basic material properties of technical and aesthetical relevance: compressive strength development, workability, setting time and colour. The performance of the test mortars was assessed together with the environmental impact of acid washed and SSA as-received by comparing the concentration levels of toxic elements and values of eluate present in the two different processed SSA with Danish limit values set for residues used in geotechnical construction work. Overall, the results of the conducted experiments showed that the compressive strength and setting time of mortar containing acid washed SSA were comparable to ordinary mortar. However, the workability and colour were exceedingly affected. The colour changed from grey to a red brown colour and the flow value of the test mortar dropped when cement was partially substituted by the acid washed SSA. Furthermore, the study revealed that several of the relevant elements measured exceeded the permissible limit values.

Keywords: Mortar, material properties, sewage sludge ash, acid extraction, phosphorous

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1. Introduction:

Utilization of sewage sludge ash (SSA) in cement based materials as partial cement replacement may be beneficial when the emission of CO_2 related to cement production is taken into consideration. Depending on the type and age of technology applied at the cement plant, app. 0. 92 ton of CO_2 [1] is produced for each ton of clinker. As a consequence, cement production is responsible for app. 5-7 % of the global emission of CO_2 [2–4]. Use of SSA as partial cement replacement could lower this emission. SSA is however, a rich source for phosphorous which is a nutrient necessary for crop growth [5, 6]. Since the existing sources for phosphorous in fertilizer production are depleting, phosphorous depletion is identified as an important issue to solve to sustain food security globally [6]. As a consequence it is essential to address SSA as a resource for phosphorous simultaneously with the potentials of utilizing SSA in cement based materials for the purpose of lowering the environmental impact of cement production.

Studies have been initiated for the purpose of investigating the possibilities to utilize SSA as-received in cement based materials. Reviews of conducted research are found in the studies of [5,7, 8]. In general, SSA is characterised as a material consisting mainly of SiO_2, Al_2O_3, Fe_2O_2 and CaO and with a high content of P_2O_5. The morphology of SSA is characterised by coarse and porous particles which has shown to decrease the compressive strength development and affect the workability of the mortar [7, 9, 10].

The overall discussion of the conducted studies have addressed the question of the pozzolanic activity of SSA and whether it is, equal to other industrial residues, suitable as supplementary cementitious material. In the review by [8] 157 different samples of SSA from 76 studies were plotted into a ternary diagram which for the majority showed that the content of relevant SiO_2, Al_2O_3 and CaO were within bounds of the latent hydraulic and pozzolanic region. In the study of [7] an assessment of 32 studies lead to the conclusion that the content SiO_2 and Al_2O_3 were less than 50% which was significantly lower than other classical admixtures such as coal fly ash, silica fume or metakaolin. The conducted experiments designated to determine the pozzolanic activity of SSA have kept the discussion going and led to ambiguous conclusions about the different parameters that possibly can inflict upon the reactivity of the SSA; temperature during curing [9]; the processing, the fineness and the chemical composition of the specific SSA [10, 11]. Another aspect which has contributed to the discussion of the pozzolanic activity and whether SSA belong to the category of

pozzolanic materials or not, is the fact that different determination methods provide different results [7, 8, 12].

Yet, the majority of the conducted studies have singly focused on the utilisation of SSA as received without confronting the fact that SSA is a potential source for phosphorus which could be retrieved if sufficient recovery methods are developed. Previously, only one study (to the authors' knowledge) by Donatello et al. [11] has examined the pozzolanic activity of sulfuric acid treated SSA and compared it to the pozzolanic activity of SSA as-received and milled SSA. The results of the study showed that the sulfuric acid affected the pozzolanic activity of the SSA, and the compressive strength of mortar containing acid washed SSA was found to be lower than for mortar containing milled SSA but higher than the compressive strength of mortar containing SSA as-received.

In this study phosphorous was extracted by means of HCl, which in previous study had shown to be an efficient method to provide a soluble, high quality calcium phosphate product suitable as fertilizer [13]. The aims of the present study were to investigate 1) technical, 2) environmental 3) aesthetical aspects, which could unfold potentials and restrictions attached to mortar containing acid washed SSA.

2. Materials and methods:

2.1 Experimental test materials:

The investigated SSA was provided by BIOFOS, a municipal owned wastewater company operating in the Copenhagen area, Denmark. The SSA was taken from one of its wastewater treatment facilities in Avedøre. It was collected directly from the process line and stored in sealed plastic containers at room temperature (sample named $SSA_{received}$). The wastewater plant processes wastewater from 255.000 person equivalents (PE) with a subsequent ash production of app. 2500 tons annually. Phosphorous is removed from the wastewater by chemical precipitation primarily with Fe. The dewatered sludge is incinerated in a fluidized bed combustor at about 850°C and the resulting ash has a red brownish colour.

The cement which was used for mortar preparation was a CEM II/A-LL 52.5R with a content of no more than 20 % of limestone filler. This particular cement was chosen because the content of

limestone filler is an additional step towards the reduction of CO_2 related to clinker production. The sand was a natural sea sand 0-4mm with technical specification following DS/EN 12620 (2008) [14]. For determination of setting time, a finer sand 0- 2 mm was used in order to limit errors to occur during the test.

2.2. Acid wash and milling

HCl was used to extract phosphorous from the SSA: 250 g of SSA were weighed into 1 l plastic bottle and mixed with 425 ml distilled water before 325 ml of concentrated HCl (37%) was added to the slurry. The plastic bottle was sealed, shaken for 10 min before the slurry was filtered through 30 µm filter paper under vacuum. The remaining solids were rinsed in 425 ml distilled water (shaken in a plastic bottle) and then filtered again under vacuum. The solids retained from the filter were dried for 24 hour at 50 ˚C and hand crushed by using a mortar and pestle to the point where no major coagulation was left. The hand crushed residue was stored in an oven at 50 ˚ (one week) (to ensure complete evaporation of water in the material). The dried residue was then milled at different time intervals into 6 fractions (0 sec, 10 sec, 30 sec, 3 min, 6 min, and 10 min) by a vibratory cup mill (FRITSCH – Pulverisette 9). The $SSA_{received}$ was dried at 50˚ for 24 hours before it was milled into the same 6 fractions as the acid extracted SSA (SSA_{acid}).

2.3. Analytical procedures:

Characterisation of $SSA_{recieved}$, SSA_{acid} and cement (test materials) included determination of water content, pH, conductivity, water solubility, loss on ignition, total concentration of trace elements and eluates. The results documented in this study were based on a triple test determination. However, a double test was used to determine the water content, pH, conductivity and loss of ignition for $SSA_{acid.}$

The water content was found as weight loss by dying the test material at 105˚ for 24 hours. The pH and electrical conductivity were measured by suspending 10.0 g of test material in 25 ml distilled water. After 1 h agitation pH and electrical conductivity were measured directly in the suspension by Radiometer electrodes. Loss on ignition (LOI) was determined both at 550˚C and 950 ˚C, and for both temperatures applied LOI was found after 30 min of heating at max temperature. Grain size distribution was determined on the basis of dry material with laser diffractometry. Solubility in water was evaluated by adding 100 g test material in 500 ml distilled water and agitate the suspension for 1 min. After settling the water was decanted and 500 ml new distilled water was

added. This was repeated and the ash was washed three times. Finally the suspension was filtered, dried and finally weighed. For SSA_{acid} 10 g and 150 ml water was used for measuring the water solubility and was only washed one time.

The concentrations of trace elements in the test materials were measured by following the description in DS/EN 259 [15]: 1.0 g material and 20.0 ml (1:1) HNO_3 was digested at 200 kPa (120 °C) for 30 min. The material was filtrated through a 0.45 µm filter after the digestion, and the solution was used for analysing the content of the trace elements (Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Se, Zn). The concentrations in the filtrate were measured by ICP–OES (Induced coupled plasma – optical emission spectrometry). Hg was measured on the solid samples after digestion by HNO_3 by ICP-MS (Induced coupled plasma – mass spectrometry) by an external laboratory. Cr (VI) was measured after extraction by colormetrically UV-VIS spectrophotometry by an external laboratory. Major oxides composition was estimated from semi quantitative analysis by X-ray fluorescence (XRF) on powder samples.

Leaching experiments were following the procedures as described in DS/EN 12457-3 part 1 [16]: 40 g of the test material and 80 g of distilled water were mixed, and shaken for 6 hours on an end-over shaker before vacuum filtration through a 45 µm filter. For SSA_{acid} only 10 g was mixed in 20 g of distilled water. The filtrate was divided into two subsamples. One subsample was used for measuring anions by an ion chromatography (IC) and the other subsample was used for analysing the concentration of heavy metals and minor elements by ICP-OES. Hg was measured by ICP-MS by an external laboratory.

Buffering capacity is defined as the ability of a material to resist changes in pH. Acid buffering capacity of the $SSA_{recieved}$ and SSA_{acid} was assayed by titration and followed the same producers described by Reddy et al. [17]. A suspension of SSA in water (6.7% w/v) was stirred for 30 min and the pH was analysed. Successive 1ml additions of concentrated HCl were made every 30 min and pH was measured thereafter. This procedure was repeated until the pH value was constant.

2.4. Mortar preparation and tests:

In this experimental study mortar containing SSA_{acid} (M-SSA_{acid}) was compared to mortar containing $SSA_{received}$ (M-$SSA_{received}$).The mortar mixes consisted of 25 % binder and 75 % sand and a water/binder ratio of 0. 5 Two test series were produced one with SSA_{Acid} (M-SSA_{acid}) and one with $SSA_{received}$ (M-$SSA_{received}$). Each series consisted of seven mixes (table 1). For six of the seven mixes 20 % of cement was replaced by the milled SSA. One mix was an ordinary mortar without any cement replacement (Reference). The mixing and casting procedures followed DS/EN 196-1 [18]. For determination of the compressive strength six specimens of each test mortars were tested. The specimens were cured in water for 28 days vertically placed in a sealed plastic box.

Table 1 Recipe for test mortars

Labelling	SSA*	Milling interval	Cement	Sand	Water
Reference	÷	÷	450 g	1350 g	225 g
M-(…*)0 sec	90 g	0 sec	360 g	1350 g	225 g
M-(…*)10 sec	90 g	10 sec	360 g	1350 g	225 g
M-(…*)30 sec	90 g	30 sec	360 g	1350 g	225 g
M-(…*)3 min	90 g	3 min	360 g	1350 g	225 g
M-(…*)6 min	90 g	6 min	360 g	1350 g	225 g
M-(…*)10 min	90 g	10 min	360 g	1350 g	225 g

* either $SSA_{received}$ or SSA_{acid}

Determinations of setting time were performed using Vicatronic automatic recording apparatus (Matest). The test performance followed the procedures of DS/EN 196-3 + A1 [19] designated for determining the setting time of cement paste. However, in order to economise with the available test material the procedure of DS/EN 196-3 + A1 [19] was used on mortar samples, and to fulfil the function as filler a 0 - 2mm sand were used. A plastic container (105 x 40 mm] was uniformly filled immediately after mixing, and the test was started. During the each test 86 penetrations were performed with an interval of 10 minutes. The distance between two penetrations was minimum 10 mm. The initial setting time was found as the first time the needle penetrated the sample 6±3 mm and the final setting time was found as the first measurement where the needle penetrated only 0.5 mm of the sample [19].

The workability, defined by the flow value of the mortar, was measured by using a flow table as described in DS/EN 1015-3 [20]. From each of the seven mixes two samples were produced to perform two tests. A truncated conical mould (50 mm of height, internal diameter of 100 mm at the bottom and 70 mm at the top) was uniformly filled with mortar and exposed to jolting by slowly raising the mould by 2 cm vertically and dropping it, 15 times at a rate of one pr. second. The flow value of each mortar was found firstly by measuring the diameter of each test samples in two directions crossing orthogonal each other and secondly by calculating the mean diameter of each test. If the mean diameter of the two tests didn't exceed more than 10%, the mean diameter of the second test sample was reported as the flow value of the mortar. Excess of mortar used for determination of the flow value was used for producing colour samples. The samples for evaluation colour were mixed after the same recipe, but were casted in moulds (100 × 100 × 30 mm internal dimensions) made of film faced ply wood.

3. Results and discussion

3.1. Test material characterisation

Table 2 gives the characteristics of the test materials, table 3 total concentrations of trace elements and tabel 4 leaching concentrations of the test materials. From table 2 it shows that the characteristics of SSA were significantly affected by the HCl extraction. Firstly, the pH was changed from alkaline to acidic. The change in pH was accompanied by a change of the conductivity which consequently increased by a factor of 15. Furthermore, the extraction of the SSA decomposed the remaining solid and led to higher water solubility, higher loss of ignition and significant changes in the concentration levels of trace elements and values for eluate.

Table 2 $SSA_{receieved}$, SSA_{acid} and cement characteristics

	$SSA_{received}$	SSA_{acid}	Cement
Water content (%)	0.31	8.89	0.28
pH	9.29	1.94	12.6
Conductivity (mS/cm)	2.42	38	13.7
Water solubility (%)	1.54	16.6	
LOI (%) 550˚	0.5	10.6	0.83
950˚	1.55	14.9	7.04

The total concentrations of major and minor trace elements and eluates for $SSA_{received}$, SSA_{Acid} and cement are shown in table 3 together with the limit values set by Danish regulations [21]. The limit values fall into three categories. Residues are categorized first by examining whether the residue meets the requirements for Category 1 (C1) for solid content and concentrations in eluate of trace elements. If the values exceed the limit values of Category 1, these are compared to the values given in Category 2 (C2) and Category 3 (C3). The three categories determine if, where and for which purpose the residues can be used in geotechnical constructions without any further permission. Those values which exceeded the permissible limits are marked dark grey in the table. By the HCl extraction of the SSA the concentrations levels of Al, Ca, Cd, Cu, Fe, K, Na, Mg, Mn, Na, P and Zn decreased, whereas the concentration of As, Ba, Cr, Cr VI, Hg, Ni, and Pb increased. The concentrations levels that exceeded the permissible limit values of Category 3 were Cd, Cu, Hg, Ni, Pb and Zn for $SSA_{received}$ and only included Hg, Ni, Pb and Zn for SSA_{acid}. All relevant concentration levels found for cement were below the limit values set for Category 1.

Table 3 Trace element concentrations in $SSA_{receieved}$, SSA_{acid} and cement

Trace elements (mg/kg)	$SSA_{received}$	SSA_{acid}	Cement	C1	C2	C3
Al	32000 ± 678	17700 ± 465	18600 ± 3850			
As	9.59 ± 1.05	0.42 ± 0.47	10.8 ± 2.67	0-20	>20	>20
Ba	724 ± 23.3	1410 ± 25	240 ± 45			
Ca	124000 ± 3980	17400± 89	360000 ± 81200			
Cd	2.77 ± 0.08	0.43 ± 0.04	0.45 ± 0.16	0-0.5	>0.5	>0.5
Cr	40.2 ± 1.17	61.3 ± 1.38	26 ± 4.85	0-500	>500	>500
Cr VI	0.5	2.4	3.6	0-20	>20	>20
Cu	590 ± 20.4	359 ± 11.4	67.5 ± 13.1	0-500	>500	>500
Fe	74300 ± 1300	76800 ± 2490	16900 ± 3210			
K	6140 ± 153	4130 ± 58.8	2650 ± 575			
Hg	4.33	7.73	0.4	0 - 1	> 1	> 1
Mg	16000 ± 371	4150 ± 103	2840 ± 529			
Mn	688 ± 12.9	285 ± 6.71	127 ± 24.1			
Na	3440 ± 104	1480 ± 50.6	1210 ± 231			
Ni	60.9 ± 1.8	71.7 ± 1.36	27 ± 5.55	0 - 30	> 30	> 30
P	126000 ± 3160	14400 ± 266	876 ± 167			
Pb	172 ± 4.89	234 ± 7.67	22 ± 4.89	0 - 40	> 40	> 40
Se	6.16 ± 3.15	7.31 ± 1.35	4.54 ± 1.97			
Zn	2100 ± 52.8	1890 ± 52.9	115 ±22	0-500	>500	>500

Three out of the fourteen elements: SO_4, Ba, and Se, exceeded the permissible limit values of Category 3 for the eluate from $SSA_{received}$, as shown in table 4 . This number increased to nine for SSA_{acid} and comprised: Cl, SO4, Ba, Cd, Cu, Cr, Hg, Mn, Na, Ni, Pb and Zn. For cement only the two elements Se and Ba were above the permissible limit values of Category 3. The eluate values measured for SSA_{acid} showed that the measured elements became progressively more mobile due to the acidic pH. In fact, a decrease in the eluate concentration was only observed for As and Se, and it was only the eluate of Se, which reached below the permissible limit values of Category 3. Furthermore, the results confirm an expected significant increase in chloride by the use of HCl. However, the extraction of P by means of HCl was effective since nearly 90 % P was removed from the SSA.

Table 4 Leaching concentrations of metals and major element from $SSA_{receieved}$, SSA_{acid} and cement

Leaching (ug/l)	$SSA_{received}$	SSA_{acid}	Cement	C1	C2	C3
Cl	23300 ± 437	23900000 ±309000	130000 ± 5500	0 - 150000	0 - 150000	150000 - 3000000
SO_4	2520000 ± 78700	2610000 ± 137000	21400 ± 2000	0 - 250000	0 - 250000	250000 - 4000000
Na	210000 ± 6610	375000 ± 9340	707000 ±15700	0 - 100000	0 - 100000	100000 - 1500000
Al	527 ± 322	140000 ± 44900	590 ±772			
As	21.7 ± 1.48	<20[i]	<20[i]	0 - 8	0 – 8	0 - 50
Ba	1020 ± 1237	1360 ±13.1	11300 ± 235	0 - 300	0 - 300	300 - 4000
Ca	637000 ±18500	6490000 ± 261000	54500 ± 19100			
Cd	<20[i]	178 ± 0.62	<20[i]	0 - 2	0 - 2	2 - 40
Cr	0.18 ± 0. 32	135 ± 1.31	40. 9± 1.8	0 -10	0 - 10	10 - 500
Cu	4.43 ± 0. 89	78300 ± 696	7.28 ±1.05	0 – 45	0 - 45	45 - 2000
Fe	<2000[i]	26700 ±361	<2000[i]			
K	145000 ±3380	848000 ± 24900	1480000 ± 24400			
Hg	<1[ii]	128	<1[ii]	0 – 0.1	0 – 0.1	0.1 - 1
Mg	187000 ±4380	1110000 ± 11542	<2000[i]			
Mn	9.57 ± 4.15	63100 ± 422	<20[i]	0 - 150	0 - 150	150 - 1000
Ni	<20[i]	6690 ±8.89	0. 82 ± 0.71	0 - 10	0 - 10	10 - 70
P	<2000[i]	39500 ±312	<2000[i]			
Pb	<20[i]	273 ± 6.99	<20[i]	0 - 10	0 - 10	10 - 70
Se	507 ± 6.47	26.9 ± 16.7	38.3 ± 9.15	0 - 10	0 - 10	10 - 30
Zn	<20[i]	319000 ± 10500	<20[i]	0 - 100	0 - 100	100 - 1500

[i] below ICP standards [ii] below limit of detection

In table 5 the major oxides from the XRF analysis in $SSA_{recevied,}$ SSA_{acid} and cement are listed. The review provided by [7] reports oxide content of other SSAs. These data were taken from between 31 and 80 oxide content values of SSA found in 31 studies. In the present study, the order by content of major oxides for $SSA_{received}$ was: CaO, P_2O_5, SiO_2, Fe_2O_3, and Al_2O_3, and for SSA_{acid} it was: Si_2O, Fe_2O_3, CaO, Al_2O_3 and P_2O_5. Due to the acid washing the content of CaO and P_2O_5 decreased significantly by a factor of five and seven, respectively, whereas the content of SiO_2 increased to the double. An increase in the content of Fe_2O_3 was also seen. In comparison to cement

the content of CaO was significantly lower for $SSA_{received}$ and subsequently even lower for SSA_{acid}. The CaO was removed by the acid washing and increased the amount of SiO_2. The content of SiO_2 in SSA_{acid} reached the mean value for SSA found in the literature, whereas the content for $SSA_{received}$ was closer to the minimum value. The content of Al_2O_3 was below the mean value for both types of SSA, but the content of P_2O_5, was for $SSA_{received}$ close to maximum values, whereas it successfully reached the minimum value after the acid washing. The change in the composition of major elements could qualify SSA_{acid} as supplement to cement since SiO_2 in combination with Al_2O_2 are important for the pozzolanic activity of the material [7].

Table 5 Major oxide complexes

%	SSAreceived	SSAacid	cement	*mean	*min	*max
Al_2O_3	8.31	6.99	4.91	14.2	4.4	34.2
CaO	21	3.78	65.8	14.8	1.1	40.1
Fe_2O_3	15.7	20	5.43	9.2	2.1	30.0
K_2O	1.69	1.93	0.81	1.3	0.1	3.1
MgO	2.32	1.18	0.53	2.4	0.02	23.4
MnO	0.09	0.01	0.04	0.3	0.03	0.9
Na_2O	1.2	2.7	<0.67	0.9	0.01	6.8
P_2O_5	20.6	2.98	0.23	11.6	0.3	26.7
SiO_2	18.6	36.4	20.1	36.1	14.4	65.0
SO_3	1.92	0.77	4.74	2.8	0.01	12.4
TiO_2	0.88	1.55	0.35	1.1	0.3	1.9
Cl	0.02	5.0	0.10			

* SSA literature [7]

The acid buffering capacity of $SSA_{received}$, SSA_{acid} and cement are plotted (figure 1). SSA_{acid} had no buffering capacity as it was already acidic due to the acid wash. For $SSA_{received}$, the pH decreased fast by the first addition of HCl from about 8 to 4, and it seems as if there is an active buffering system in $SSA_{received}$ at just above pH 2 as it took an addition of 11ml to reach a pH below 2.

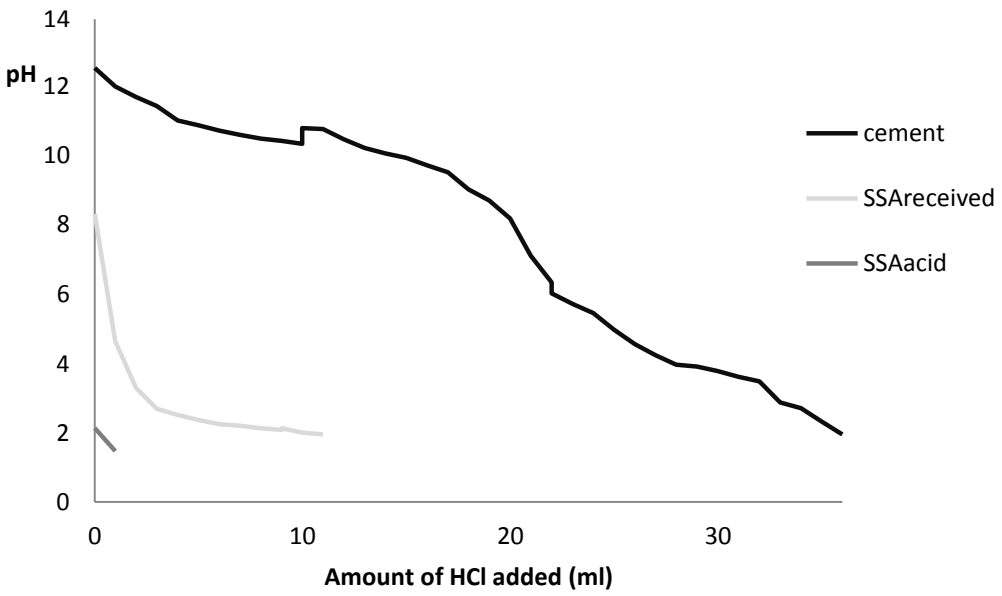

Figure 1 Buffer capacity for $SSA_{received}$, SSA_{acid} and cement

Particle size distributions for $SSA_{received}$ milled in interval 0 sec -10 min were homogenously distributed (figure 2a). The fineness of the particles increased when the duration of the milling increased. Furthermore, the curves for all fractions of $SSA_{received}$ were similar to the curve shape of cement. The curve for SSA_{acid}10 sec was uneven and did not resemble the curve of the particle size distribution for cement (figure 2b), and as 10 sec is the shortest milling time tested, it seems as if this milling time is too short to obtain a smooth grain size distribution curve.

The volume of particles under the size of 100 µm was much higher for the unmilled samples SSA_{acid}0sec than for the corresponding references $SSA_{received}$ 0sec. At 50 % of volume the maximum particles size for SSA_{acid}0sec was 50 µm (figure 2b) and approximately 120 µm for $SSA_{received}$0sec (figure 2a). Figure 2a shows that for $SSA_{received}$ the maximum particle size of 50 µm at volume of 50 % was obtained between time intervals 10 – 30 sec. It is important to notice that the actual grain size distribution for SSA_{acid} can be discussed since the water solubility of SSA_{acid} was rather high (16.6 %) when comparing it to $SSA_{received}$ (1.54 %). The soluble fraction of SSA_{acid} might be due to the formation mainly of salt crystals which was induced by the use of HCl to extract phosphorous. In the dry material the soluble crystals could completely dissolve, attach to the surface of insoluble particles or precipitate as crystals independently distributed in the $SSA_{acid,}$ which would both influence on the particle size distribution.

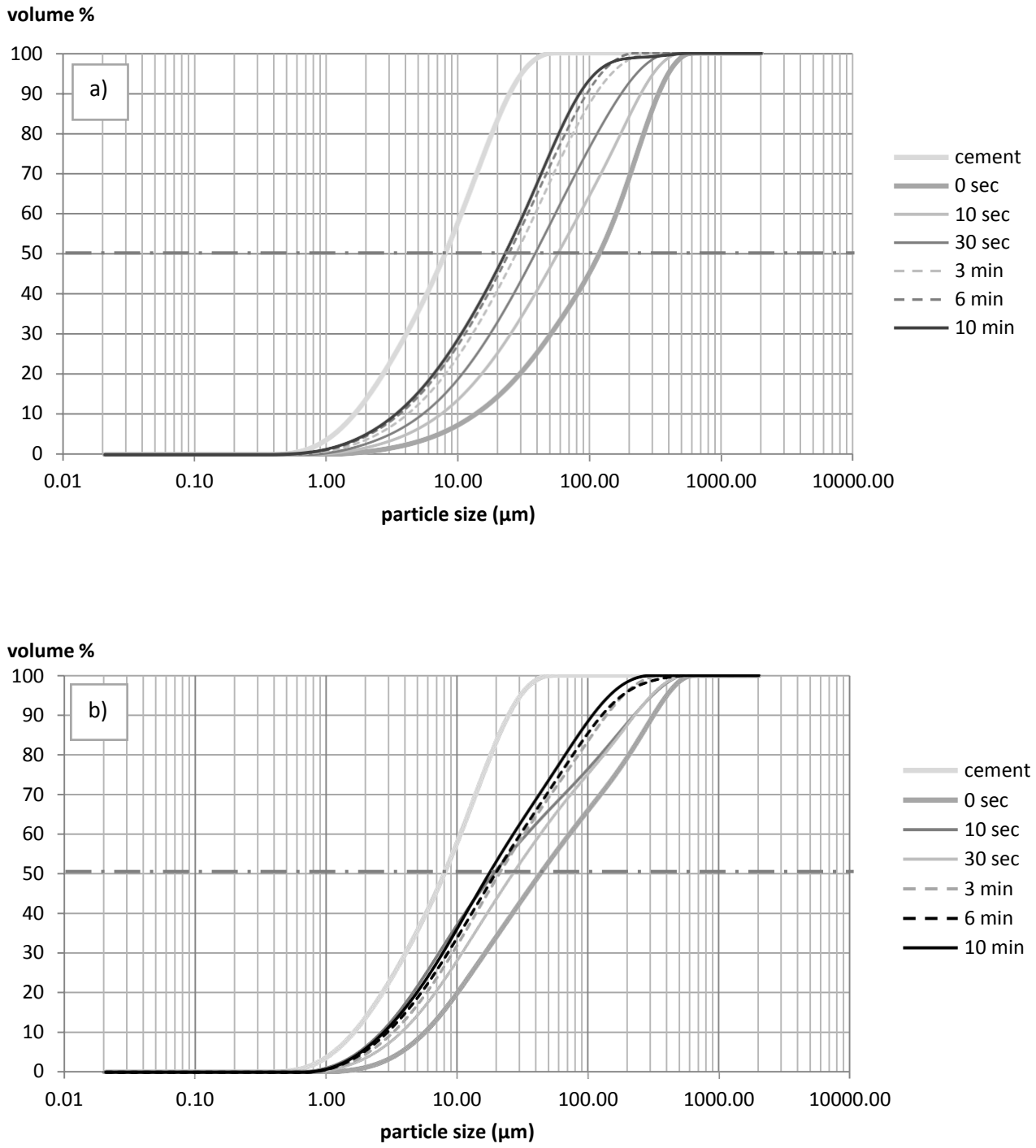

Figure 2 Particle size distribution curves for a) $SSA_{received}$, b) SSA_{acid} compared to cement

3.2. Mortar testing

3.2.1. Compressive strength

The compressive strength at 28 days for mortar samples containing 20 % of $SSA_{received}$ or SSA_{acid} are compared in figure 3. Two references of each series were produced. In the figure the references carry the colour of the series they belong to. This is due to the curing conditions as it was expected that leaching from the two series were different and would provide different curing environment. Thus, the two series were intentionally separated during curing in order to limit parameters inflicting on the results. Whether the minor difference between the two references was due to differences in the curing conditions cannot however, be concluded on the basis of the existing result. However, from the figure it can be derived that the acid washing of the SSA had a positive effect on the compressive strength development. For $M\text{-}SSA_{received}$ the ash needed to be milled between 3 – 10 min in order to obtain comparable compressive strength development as ordinary mortar without any substitution of cement (Reference). The compressive strength dropped relatively dramatically for $M\text{-}SSA_{recieved}$ 0sec compared to the reference. Contrarily, the compressive strength for mortars containing SSA_{acid} were almost comparable to the reference regardless of that SSA_{acid} was also milled into the same 6 different fractions. Only a small drop in compressive strength was seen for $M\text{-}SSA_{acid}$ milled in the intervals 0sec –30 sec.

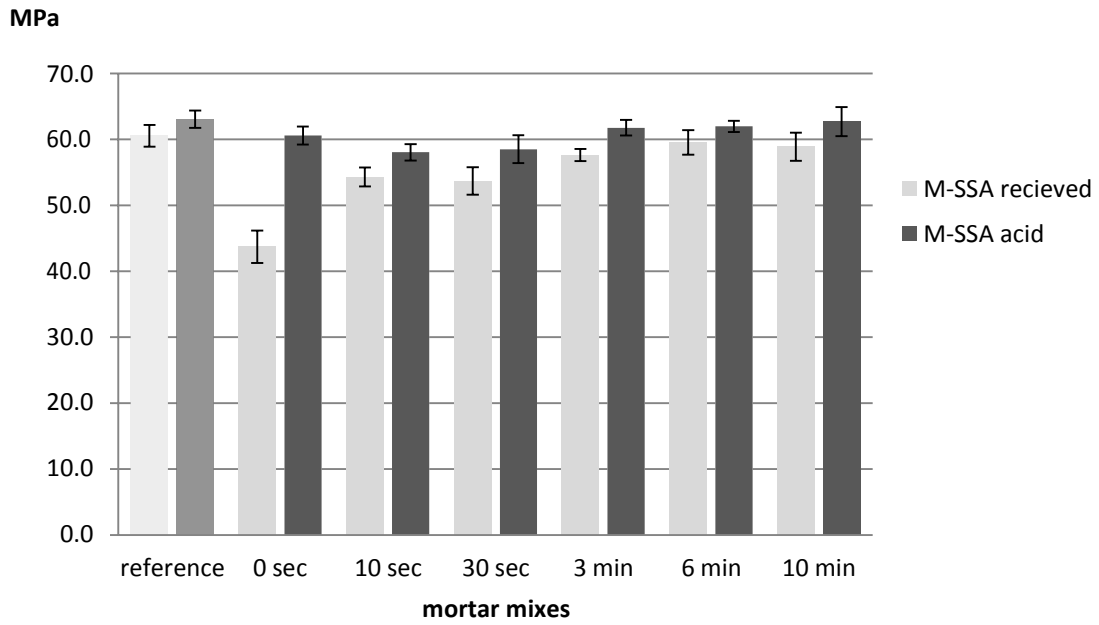

Figure 3 Compressive strength 28 days for $M\text{-}SSA_{received}$, $M\text{-}SSA_{acid}$ and reference

3.2.2. Workability

The workability of the test mortars was determined from the flow value (FV) (figure 4). The flow value is expressed by the value of test 2 (second test conducted) when the value of test 2 did not differentiate more than 10 % from the value of the test 1 (first test conducted). In figure 4 the results of both tests (test 1 and 2) are included because they display the implication of time spend during test performance and how it influenced the flow value. In this way the results for mixes M-SSA_{acid} had a significant loss of consistence between the two test performances. This reveals that SSA_{acid} due to the acid washing initially was much more reactive than $SSA_{received}$. In general, the flow values for mixes M-$SSA_{received}$ and M-SSA_{acid} did not at any time reach the same flow value as the reference. However, the results in figure 4 shows that the process of the milling $SSA_{received}$ and SSA_{acid} was as an important parameter for the flow value as it increased parallel to an increase of the time applied to the milling. The flow values found for M-$SSA_{received}$ increased stepwise and for M-SSA_{acid} it increased somewhat gradually. However, the largest flow value which was found for M-SSA_{acid} was the flow value of M-SSA_{acid}10 sec. This flow value stands out and suggests either an error or that the specific SSA_{acid} had obtained an optimal grain size distribution. However, an irregular behaviour of SSA_{acid}10 sec was also seen in the analyses of the particle size distribution as the curve was uneven and less smooth than the particles size distributions of un-milled SSA_{acid} (SSA_{acid}0sec) and SSA_{acid} milled in intervals between 30sec - 10 min.

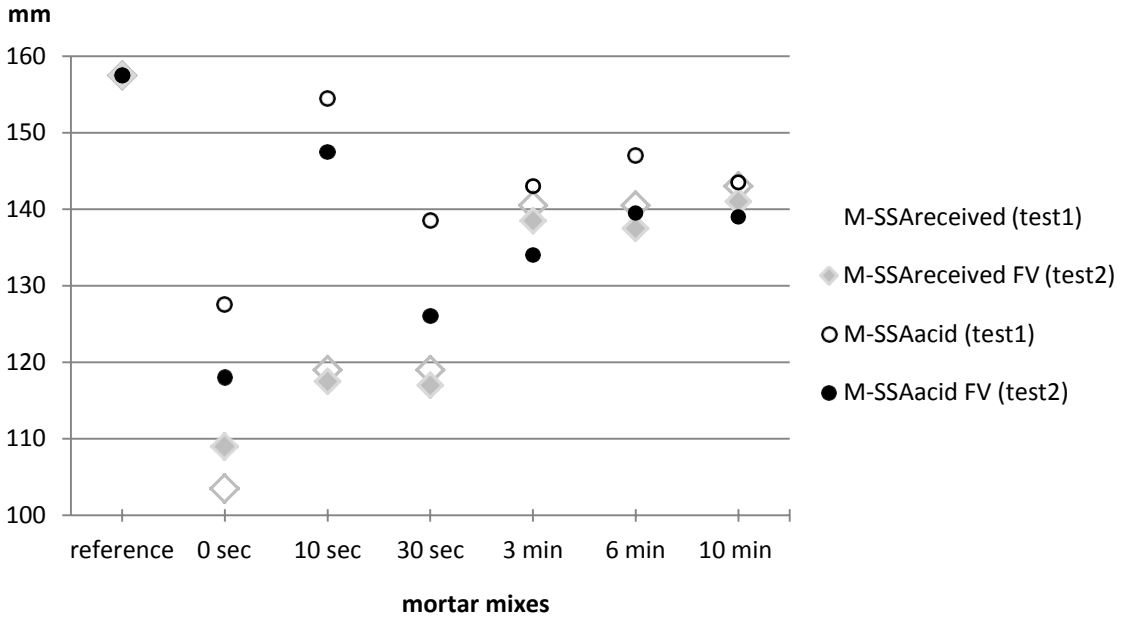

Figure 4 Flow value for M-SSA$_{received}$, M-SSA$_{acid}$ and reference

3.2.3. Setting time

The setting process for the different mortar samples are shown in figure 5, with initial and final setting times shown in table 6. The initial setting time for M-SSA$_{acid}$ occurred much faster than for M-SSA$_{received}$, and closer to the initial setting time of the reference. This can be seen in figure 5 in which selected graphs for M-SSA$_{received}$ and SSA$_{acid}$ together with the graph of the reference are displayed for comparison. Generally, for M-SSA$_{received}$ the graphs monitoring the phase change were much more uneven than it was seen for M-SSA$_{acid}$. This may be due to the fact that the mixes containing SSA$_{received}$ were less workable and thus less fluid, which may have contributed to the occurrence of voids in the mortar and thus, allowed the needle to fall free during test execution. However, irregularities were also seen for mixes of M-SSA$_{acid}$, particularly M-SSA$_{acid}$0sec.

The initial setting time nearly doubled for M-SSA$_{received}$0sec when comparing it to the initial setting time of ordinary mortar. However, from the results it can be seen that the milling had an impact on the setting time for both types of mortars M-SSA$_{received}$ and M-SSA$_{acid.}$ .The reactivity increased in conjunction with the time applied to the milling process. However, even though the milling of SSA$_{recieved}$ shortened the setting time to some extent, the setting time did not at any point resemble the lower setting time of the reference mortar and M-SSA$_{acid}$. The impacts of phosphate on the hardening process of cement have previously been studied [22, 23]. The study of Lin et al. [23]

investigated options to replace raw materials in clinker production with different types of SSA. The study documented that the setting time significantly increased when the amount of phosphate in cement increased by 0.85%. The results of the present study comply with this trend.

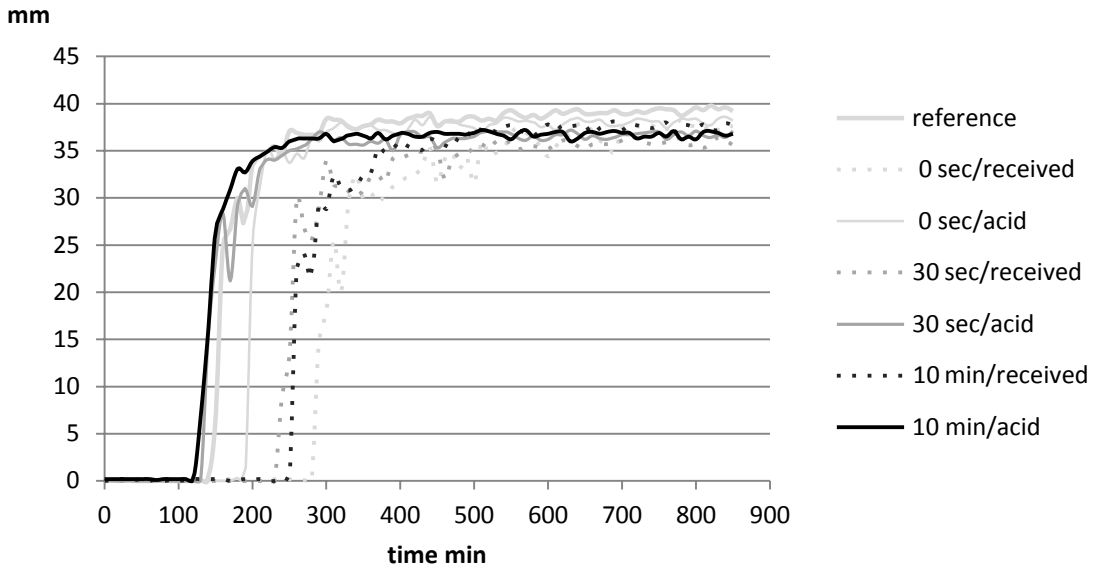

Figure 5 Setting process for selected M-SSA$_{received}$, M-SSA$_{acid}$ and reference mortar

Table 6 Initial and final setting times for selected M-SSA$_{received}$, M-SSA$_{acid}$ and reference mortar

Sample	Initial setting time (min)	Final setting time (min)
Reference	150	550
0 sec/received	290	640
0 sec/acid	200	420
30 sec/received	240	530
30 sec/acid	140	400
10 min/received	260	550
10 min/acid	130	300

3.2.4. Colour

The effect of SSA$_{received}$ on the colour of the samples was much less distinct than for the samples with SSA$_{acid}$. In figure 6 the two series are collectively displayed. SSA$_{received}$ induced slightly darker tones as the fineness of the particles increased due to the milling. The same colour development was not seen for the M- SSA$_{acid}$. The colour was much more significant and the colour was the same for all samples containing SSA$_{acid}$. Thus, the fineness of the particles of SSA$_{Acid}$ did not influence the

colour as it was seen for the M-SSA$_{received}$. The brown reddish colour of the SSA$_{received}$ can be related to the high content of iron. For SSA$_{acid}$ the content of iron increased as seen in the XRF analysis (table 3) and at the same time Fe became unstable as the leaching tests showed (table 2). The significant colour change of M-SSA$_{acid}$ suggests that Fe formed new complexes e.g. anionic ferric chloride complexes [24] which in a solution could have generated the saturated reddish colour.

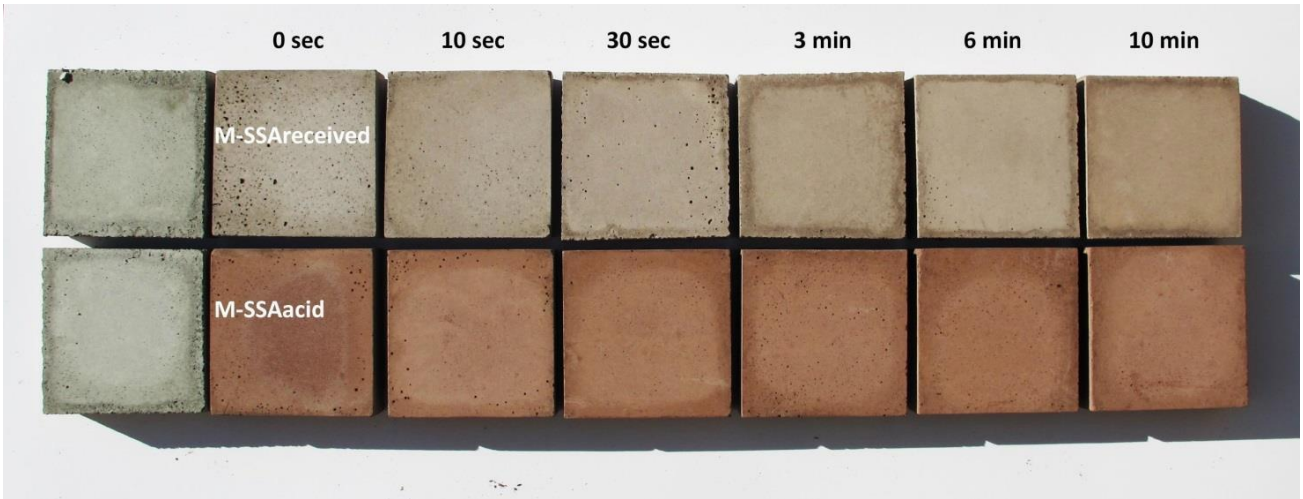

Figure 6 colour samples of M-SSA$_{received}$, M-SSA$_{acid}$ and reference

3.3 Technical, environmental and aesthetical potentials and constraints

3.3.1. Technical aspects

The milling of the SSA was of significant importance for the compressive strength development of M-SSA$_{received}$. Milling of SSA has shown to have a positive effect on the compressive strength development and on the pozzolanic reactivity [10, 11]. In the study of Pan et al. [10] a compressive strength development was correlated to the size of the outer surface area of SSA particles and even though the fineness of the particles increased due to the milling, the specific surface area did not increase to the same extend. Thus, it was suggested that the porous particles of SSA had many open pores and that these open pores are blocked during early hydration and the pozzolanic reactivity is only promoted at the outer surface of the particles. Donatello et al. [11] showed that the compressive strength of mortar containing milled SSA reached 96 % of the compressive strength of reference mortar, which resembles the result found in the present study in which the M-SSA$_{received}$10min reached app. 98% of the strength. The d_{50} was 119 µm in the present study and

106.8 µm for SSA used in study of Donatello et al. [11]. However, the particle size distribution of the milled SSA in this and the study of Donatello et al. [11] were not comparable as d_{50} was 23 µm for $SSA_{received}$10 min against 4.8 µm regardless of a longer milling time in the present study. Thus, it may be possible that the reactivity of SSA is not only related to physical changes and an increase of the specific surface area but also to a transformation of the material's chemical and physiochemical composition induced by the mechanical energy applied or mechano-chemical treatement. Mechano-chemical treatment methods have been investigated for the purpose of preparing new construction materials [25] and to modify waste materials to qualify them for further use in construction materials [26].

The morphology of unmilled SSA is generally found to affect the consistence and the workability negatively when SSA is used to partially replace cement in mortar corresponding to a higher water demand for mixes containing SSA as received [7, 11, 27]. The increase of the flow value which was seen for mortar with milled $SSA_{recevied}$ supplemented the findings of Donatello et al. [11]. In the study it was found that the water demand was lower for mixes containing milled SSA. Since the water/cement ratio is the single most important parameter for the strength development, the reduced water demand for mortar with milled SSA consequently has a positive effect on the final compressive strength[11]. However, other factors related to the milling of the SSA besides reduced water demand may have affected the strength development: improved filler properties and promotion of amorphous silica (a parameter relevant for the pozzolanic activity), or a combination of all three factors [11]. The compressive strength of M-SSA_{acid} did not evolve parallel to an increase of the milling time. The compressive strength of M-SSA_{acid}0sec was comparable to both the reference mortar and M-SSA_{acid}10min.

Collectively, the results of the conducted experiments all showed that HCl extraction of phosphorous promoted increased reactivity of the residual SSA. The major elemental and chemical changes of the SSA induced the rapid loss of consistence which was seen in the flow value determinations and accelerated the hardening process. The process of milling the SSA_{acid} did also affect the flow value and the setting time of the mortar as these two test parameters improved when the time interval of the milling increased.
The compressive strength increase of M-SSA_{acid} may be related to that the reactive part of a pozzolane SiO_2 and Al was promoted by the acid washing. The content of SiO_2 increased from

18.6% to 36.4% whereas the total concentration of Al decreased. However, the leaching values for SSA_{acid} showed that the availability of Al increased as the concentration of the eluate was significantly higher for SSA_{acid} than for $SSA_{received}$. Furthermore, the high concentrations of aluminate and sulphate ions may have promoted early formation of ettringite [28] and induced the rapid loss of consistence, which was seen in the flow value experiment.

High alkalinity stabilises the hydration products formed in the cementitious system, the leaching behaviour of heavy metals and preserves the steel of reinforced concrete. If the pH drops below 11.5 the passivity of steel would be destroyed and corrosion occurs. However, an excess of chloride ions in the matrix could be destructive for the steel even at pH higher than 12 [28]. For that reason it would not be feasible to use SSA_{acid} for reinforced concrete. Furthermore, the high content of chlorides caused problems during the processing of SSA. The equipment which was used to process the SSA_{acid} corroded after having been in contact with the material. However, a high percentage (16.6%) of SSA_{acid} was soluble and it is likely that a significant amount of soluble salt crystals can be removed simply by using water. But it would be necessary to investigate this before any valid conclusions can be made.

3.3.2. Environmental aspects

Donatello et al. [29] evaluated the leaching of heavy metals of SSA as received and compared the values with the waste acceptance criteria threshold limits set by the European Union for landfill application of waste. Seven different SSAs were tested and the results showed that leaching of Mo, Se and/or Sb designated the SSA to be placed at hazardous waste landfills. This was also supported by the study of Chen et al. [27] who found that the leaching of most heavy metals was far below the limit values except for the values of Mo and Se.

In the present study the leaching behaviour of SSA_{acid} showed that the leaching increased for Cu, Cd, Hg, Pb and Zn after the acid extraction, even if the total concentrations had only slight changes for these elements before and after the acid extraction. Contrarily, the leaching of As, Ba and Se decreased after acid extraction and together with Cr leaching, were the metals that was below the Category 3 limit values. Since unlimited use of the SSA for geotechnical construction purposes requires that all values are below the Danish limit values of Category 1, and restricted use requires values below Category 3 special permission is required in order to use both SSA_{ref} and SSA_{acid} in constructions.

Heavy metals in SSA as received are stabilized and only minor leaching of heavy metals can be expected when SSA is incorporated into a cement paste [7, 27]. Leaching from monolithic concrete (replacing rate 10 % of cement and 2 % of sand) showed higher leaching of Cr, Cl and SO_4 for ordinary concrete compared to SSA concrete [27]. Whereas the level of Zn was higher for the SSA concrete and all leached metal concentrations for the SSA mortars were below threshold limits [27]. Comparing leaching from monolithic and crushed SSA mortar (replacing rate 25% and 50%) showed as expected that the leaching of heavy metals increased when the mortar was crushed [7]. As the leaching behaviour of SSA_{acid} is significantly changed in comparison to $SSA_{recevied}$, it can be expected that mortar containing SSA_{acid} would lead to higher leaching values of heavy metals.

3.3.3. Aesthetical aspects

Until now a general application of SSA-containing mortar and concrete has failed. The reason could be related to the uncertainties of the pozzolanic potentials of SSA and thus, the feasibility to utilise SSA to partially substitute for cement, or the fact that SSA contains a significant amount phosphorous. However, another obstacle may possibly be related to the variation of SSA and possible colour change when especially milled SSA is used in cement based materials. In a Danish large scale pilot project Biocrete [30] utilisation of SSA as a resource in concrete production was assessed by testing the use of milled SSA to partially substitute coal fly ash. In this project it was found that concrete containing an iron rich SSA, similar to the SSA tested in this present study, would limit the application potentials due to the red colour [30].

A previous study by Kappel et al. [31] demonstrated if unmilled SSA replaced 20% of cement in mortar the colour only slightly changed from grey to grey with a red tint. Furthermore, it was found that the colour intensity of mortar containing milled SSA increased parallel to an increase of fineness of the SSA particles. Thus, the milling of the SSA was a precondition for the colour to evolve. For mortar containing SSA_{acid} the colour change was significant as the mortar obtained a saturated red brown colour and the colour intensity did not increase when the fineness of the particles increased as it did for mortar containing $SSA_{received}$. The distinct colour of SSA_{acid} mortar may challenge the assumption that cement based materials containing SSA_{acid} is considered of secondary quality compared to ordinary mortar and concrete, but instead has aesthetical potentials which are particularly suitable for visible structures.

4. Conclusion:

There are two main concerns related to the utilisation of SSA_{acid} as cement replacement and its further use for constructional purposes. These are the large introduction of chlorides to the matrix and the high concentration levels of toxic elements and leaching values. However, mortar containing HCl washed SSA also showed aesthetical and technical potentials.

- The compressive strength of mortar containing SSA_{acid} is comparable to normal mortar at 63 MPa. A minor drop in the compressive strength to 58 – 58.5 MPa was seen for the mortar containing acid extracted SSA milled between 10 – 30 sec.

- The workability determined by the flow value of the test mortars containing SSA_{acid} and $SSA_{recevied}$ improved as finer particles were obtained by milling the two types of SSA. However, the flow value of the test mortars did not reach the flow value found for the reference mortar.

- The setting times of mortar containing SSA_{acid} were comparable to the reference mortar. The acid washing of SSA significantly reduced the setting time in comparison to the setting time of mortar with $SSA_{received}$.

- The concentration levels of toxic elements exceeded Danish limit values for several toxic elements in both SSA_{acid} and $SSA_{recieved}$. Furthermore, the concentrations in the eluate showed that the relevant elements became much more mobile by the acid extraction of the SSA, and transformed the SSA to a more instable material.

- The colour of mortar with SSA_{acid} changed from grey to a red brown colour. The milling of the SSA_{acid} did not have any visual effects, as the colour did is not change disregarding increasing duration of the milling time. The red brown colour of mortar containing SSA_{acid} was more evident in comparison to mortar containing $SSA_{received}$. The significance of the colour may expand the perception of mortar and concrete generally associated with the colour grey.

Acknowledgements

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5.3 Electrodialytically treated SSA in mortar

The focus of the third study was to examine the use of electrodialytically treated SSA in mortar. Electrodialytic separation is another method for extracting the phosphorous from the SSA before using the ash residue as partial cement replacement in mortar. This method designates from a technology which was developed at DTU for cleaning polluted soil by using the principals of electrokinetics (Ottosen et al. 1997) However, electrodialytic treatment processes have also been found suitable for separating useful elements from problematic elements in waste materials like SSA. The principal behind the method is to lower the pH in a SSA suspension consisting of water and SSA by applying a low DC current to the suspension. When pH is below 2 most of the heavy metals will be released to ions in the solution and the phosphorous uncharged. The positively charged heavy metals are attracted to the negative electrode and will move towards the cathode by passing a cation exchange membrane. As the phosphorous stays in the suspension, heavy metals and phosphorous are efficiently separated. Results of previous studies have showed that 90 % of phosphorous can be recovered from SSA (Ebbers et al. 2015; Ottosen et al. 2016).

The results of this study showed that the compressive strength decreased by 8 %, the workability was affected as the fresh mortar became dry, and the colour changed to a red earth tone for mortar with electrodialytically treated SSA compared to reference mortar. The milling of the electrodialytically treated SSA had a slight impact on the compressive strength, which increased, but it did not have any further impact on the workability or the colour of the mortar.

5.3.1 Utilisation of electrodialytically treated Sewage Sludge Ash in Mortar

(Kappel, A., Viader, R. P., Kowalski, K. P., Kirkelund, G. M., & Ottosen, L. M. (2018). Utilisation of Electrodialytically Treated Sewage Sludge Ash in Mortar. Waste and Biomass Valorization, 1-13.)

5.3.1 Utilisation of electrodialytically treated sewage sludge ash in mortar

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ABSTRACT

Phosphorous is a scarce resource and there is a need to develop methods for recovery of this irreplaceable nutrient from secondary resources, e.g. from sewage sludge ash (SSA). Today SSA is most often disposed of and the resource is lost. In the present study, about 90 % phosphorous was recovered from SSA by electrodialytic separation in a bench scale set-up, and the particulate residue after the extraction (SSA-ED) was evaluated for use as cement replacement in mortar. The SSA-ED and untreated SSA were grinded for 0sec, 30 sec and 10 min in order to obtain fractions with different degrees of fineness. Each fraction was tested as cement replacement with 20% substitution in mortar. The technical and aesthetical properties of mortars containing the two SSAs were compared to the properties of ordinary mortar. The SSA-ED was acidic; however, this did not significantly influence the mortar properties on short term investigated here. For example, the compressive strength of the mortar with SSA-ED only decreased by 8% compared to ordinary mortar. The workability of mortars with SSA or SSA-ED was reduced compared to the reference. The colour of mortar with SSA-ED was warm reddish, and more intense than the colour of the mortar with SSA. The intense colour was due to the increased concentration of hematite during ED. This study showed potential for separating SSA to two resources by combining electrodialytic extraction of phosphorous and subsequent utilize the residual mineral ash in mortar.

Keywords: SSA, electrokinetic remediation, phosphorous, heavy metal, fineness

INTRODUCTION

Sewage sludge ash (SSA) is the residue from incineration of sewage sludge at wastewater treatment plants. Phosphorous in SSA is generally not plant available, and thus the SSA has no fertilizer value and thus the common practice is landfilling of the SSA. The natural deposits of phosphorous are rapidly depleting with the current consumption rate, and in such a speed that phosphorous already today is regarded as a scarce element. This is alarming as phosphorous is an irreplaceable element for all living organisms. Drivers to find appropriate applications for SSA instead of landfilling was initially to solve a waste problem due to increasing quantities of SSA [1-3] rather than the phosphorous reuse. Extensive research was carried out for the purpose of investigating possibilities to use SSA in production of construction materials in general and in cement based materials specifically [4-6]. Over the last decade, research on SSA utilisation has developed alongside the developments of waste management policy. The overall aim of the waste hierarchy in the European directive on waste [7] is to encourage EU member states to "reintroduce as much material as

possible into production processes" [8]. By the introduction of the waste hierarchy, the conception of waste has also changed from the perception of waste as a problem to regarding waste as a resource [8]. This change is also reflected in studies on SSA utilisation, in which SSA is referred to as "secondary material" [6] and "useful material" [4]. When considering SSA as a resource, the main resource of interest in SSA is the relatively high content of phosphorous, which generally is 5 – 10 wt% [5].

In the Resource Strategy by the Danish Government in 2013, the target is to reuse 80 % of all phosphorous by 2018, including phosphorous from SSA. To reach this goal, efficient methods to recover the phosphorous from SSA are required and different methods are currently under development. The methods are grouped in two: thermochemical treatment or wet chemical extraction [4]. A drawback for the latter method is that in acid extraction the heavy metals are extracted together with the phosphorous [9, 10], which hampers the use of the recovered phosphorous in fertilizer production. To obtain a clean phosphorous product, different processes for separation of phosphorous and heavy metals have been suggested, such as pH adjustment [11, 12], sulphide precipitation [11], cation exchange [9, 11] and electrodialytic separation [13, 14]. The first three separation methods require a two-step treatment: first extraction then separation. In electrodialytic separation, the phosphorous extraction and heavy metal separation occur simultaneously.

Electrodialytic separation first developed for soil remediation, and was recently further developed for extraction of phosphorous from SSA with simultaneous heavy metal separation. Fig. 1 shows the patented two-compartment electrodialytic cell [15].

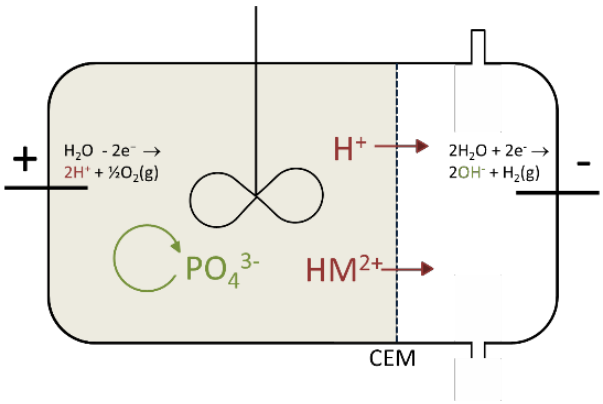

Fig. 1 The two compartment electrodialytic set-up for treating a material suspension. CEM-cation exchange membrane

The anode is placed directly in a suspension of SSA and water. The cathode is placed in a separate compartment and a cation exchange membrane separates the two compartments. When a DC current is applied, the pH of the suspension decreases as protons are generated at the anode from electrolysis. Once pH reaches below 2, P and a part of the heavy metals are extracted. The heavy metal cations electromigrate to the catholyte passing the cation exchange membrane and thus the heavy metals are separated from the suspension, where phosphorus remains. Studies by Ebbers et

al. [16] and Ottosen et al. [13] have shown that it is possible to recover more than 90% P with this experimental set-up in laboratory scale (25-50 g SSA treated) and that the extracted phosphorous is pure from heavy metals and can be processed further to fertilizer [13].

A question now arises, whether the remaining mineral residue is an additional resource. A possible application for the SSA-ED could be as cement replacement in concrete. The CO_2 emission from cement production is responsible for about 5% of the anthropogenic emission. Cement is the essential "glue" in concrete, and one way to lower the general CO_2 emission related to concrete is to use materials with pozzolanic activity or filler effect as partly cement replacement. Research combining extraction of phosphorous and using the treated SSA as cement replacement is scarce. Donatello et al. [4] studied the use of sulfuric acid to recover phosphorous from SSA and use the acid washed SSA in mortar. They found that the sulphate from the acid influenced the properties of the mortars negatively compared to the untreated SSA. SSA-ED will not contain similar high sulphate content. The aim of the present work is to investigate the potential for combining electrodialytic extraction of phosphorous from SSA and the use SSA-ED as cement replacement in mortar.

MATERIALS AND METHODS

SSA from Avedøre, BIOFOS was used in the experiments, a wastewater treatment plant operating in the Copenhagen area, Denmark. The SSA was from mono-incineration of sewage sludge and it was sampled in May 2014. Iron was used at the wastewater treatment facility to precipitate P and the sewage sludge was incinerated in a fluidized bed combustor at about 850°C.

Analytic procedures in ach characterization

Characterization was made with dried ash and cement. Concentrations of Cu, Pb, Zn and Cd were measured with ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) after pre-treatment in accordance to DS259: 1.0 g ash and 20.0 ml (1:1) HNO_3 was heated at 200 kPa (120°C) for 30 minutes and filtered through a 0.45 μm filter prior to the analysis. Ash pH and conductivity were measured by suspending 10.0 g ash in 25 ml distilled water. After 1 hour agitation pH and conductivity were measured directly in the suspension with Radiometer electrodes. Water content was measured as weight loss after 24 hours at 105ºC (calculated as weight loss over the weight of the wet sample). Loss on ignition (LoI) was found after 30 minutes at 550ºC. Five replicates of each of these analyses were made. Solubility in water was evaluated by suspending 50.0 g ash in 500 ml distilled water and agitated for 1 min, after settling the water was decanted and another 500 ml distilled water added. This was repeated until the ash was washed three times. Finally, the suspension was filtered and the ash dried and weighed. Major oxide composition was estimated from semi-quantitative analysis by X-ray fluorescence (XRF) on powder samples by an external laboratory. The particle size distribution was measured by laser diffractometry. Ash mineralogy was studied by X-ray powder diffraction (XRD), for identification of major crystalline phases. The instrument was a PANalytical X'Pert Pro operating at 45 mA and 40 kV applying Cu Kα radiation with a 2Θ X'Celerator detector. The samples were scanned in the range of 4-100 2 Θ

within 2.5 hours. The diffractograms were interpreted by using the ICDD PDF-4 database for minerals and the main peaks were identified.

Electrodialytic bench-scale experiment

Fig. 2 shows the ED bench-scale set up. It was built in a plastic container (60x40x32 cm). Two anodes were placed directly in the suspension. The cathodes were placed in cathode units, which were boxes with circulating catholyte. One side of the box (facing into the container) was a cation exchange membrane (27 x 37 cm^2) from Ionics. Both cathodes and anodes were platinum coated titanium meshes (4 x 20 cm^2).

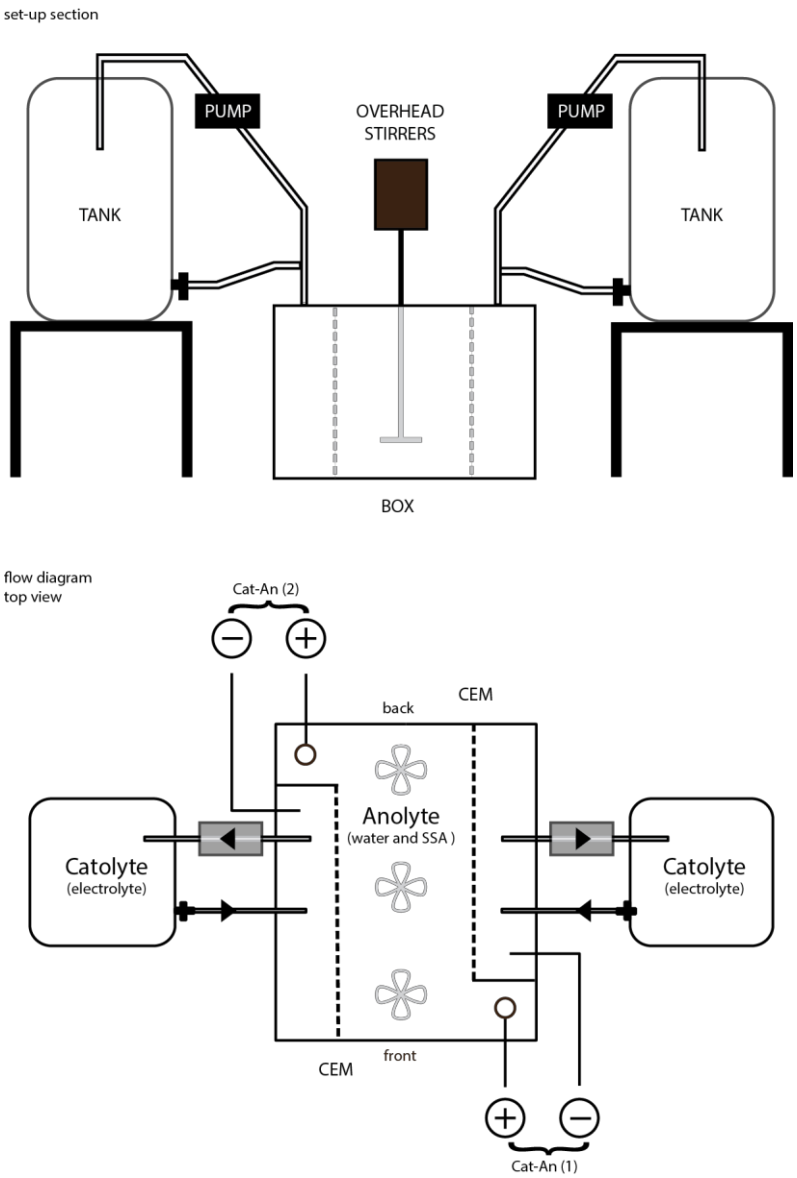

Fig. 2 The bench scale electrodialytic experimental setup, CEM-cation exchange membrane

The catholytes (25 l each) were prepared by mixing 21.5 g of $NaNO_3$ with 50 ml of 1:1 HNO_3 into 25 l of distilled water. Each of the two cathode units had a separate catholyte circulation system.

The SSA suspension prepared for the experiment had a liquid to solid (L:S) ratio of 10.3. First, 28 l distilled water was added to the anolyte compartment. Thereafter 3 kg of SSA was mixed into 3 l of distilled water in a separate tank and added gradually to the anolyte to make the full suspension. The SSA was kept suspended to avoid sedimentation in the container by three overhead stirrers (vos 14 /VWR).

A power supply (Blanko- Model Q J-3003C III) maintained a constant current. Each pair of electrodes shared the same power supply, however, independently connected to separate outlets. The duration of the experiment was 24 days and a constant current of 0.4 A was applied to each electrode pair for the first two days and 1.0 A for the remaining 22 days. The pH of the catholytes was adjusted with 1:1 HNO_3 after 2, 4, 11 and 15 days, when the pH of the catholyte was above 2. The pH and electrical conductivity (EC) were measured regularly in the SSA suspension at two places (named back and front, see Fig. 2). Samples of the SSA suspension were collected regularly, filtered, and the target elements were measured in the filtrate by ICP-OES.

After the ED experiment, the SSA suspension was filtered, dried at 50˚C until the liquid had evaporated, crushed lightly by hand in a mortar, and finally stored in sealed plastic bags. Target elements, pH and conductivity were measured in the filtrate, SSA and catholyte at the end of the electrodialytic experiment. LoI, water content, water solubility, concentrations of Cd, Cu, Pb and Zn (ICP-OES) and P (XRF) and mineralogy (XRD) were measured in the ED treated and dried ash.

Mortar preparation and testing

Before the SSA and SSA-ED (here refered to as test materials) were used in mortar, they were grinded for 0 sec, 30 sec and 10 min using a vibratory cup mill (FRITSCH - pulverisette 9). The grain size of the SSA and grinded samples are shown in Table 1. The grinded test materials were used for the production of test binders that consisted of 80 % of Cement and 20 % either SSA or SSA-ED. In total mortar 8 mixes were produced (Table 2) The basic recipe, which was used for the mortar production, was 75 % sand, 25 % binder and a water/binder ratio of 0.5. The sand was a coarse grained sea-sand (0 – 4 mm) and the cement used was CEM II/A-LL 52.5R. This particular type of cement has a reduced CO_2 footprint compared with ordinary portland cement as up to 20 % of the cement clinker is replaced by limestone filler.

Table 1 Grain distribution of the tested materials

	d10 (µm)	d50 (µm)	d90 (µm)
Cement	1.72	8.45	26.2
SSA_{0sec}	14.1	124	356
$SSA_{30\ sec}$	5.59	39.8	182
$SSA_{10\ min}$	3.54	24.1	89.0
SSA-ED	2.79	101	817
$SSA\text{-}ED_{30\ sec}$	2.22	44.1	556
$SSA\text{-}ED_{10\ min}$	1.34	9.50	142

Table 2 Recipes of the mortars. * indicating either SSA or SSA-ED

Labelling	Ash*	Grinding interval	Cement	Sand	Water
M -Ref_f	÷	÷	450 g	1350 g	225 g
M-(…*) $_{0\ sec}$	90 g	0 sec	360 g	1350 g	225 g
M-(…*)$_{30\ sec}$	90 g	30 sec	360 g	1350 g	225 g
M-(…*)$_{10\ min}$	90 g	10 min	360 g	1350 g	225 g

The mortar was prepared in a Hobart mixer with the capacity of 5 liters. Binder (either cement or cement and SSA) was placed in the bowl, and the water was added. The mixer was switched on for 30 sec at low speed. The sand was added during the next 30 sec, and then the mixer was switched to high speed and the mixing continued for another 30 sec. The mixer was stopped and the paste adhering to the inside of the bowl was within the next 30 sec removed by a scraper. After 60 sec of rest, the stirring process proceeded and the paste was stirred at high speed for another 60 sec.

The compaction procedure was executed by a vibrating table at a frequency of 53 Hz. The mortar was placed in the mould within the first 30 sec and the mortar was vibrated for another 90 sec. The mortar samples were sealed in plastic for 24 hours, demolded and cured in water vertically placed in a sealed plastic box. The two series were cured in separate boxes because the leaching of the mortars in the two series was expected to be different. M-$SSA_{0sec\ -10\ min}$ were cured for 28 days and M-$SSAED_{0sec\ -10\ min}$ for 40 days. The extended curing time applied for M-$SSAED_{0sec\ -10\ min}$ may have influenced the compressive strength result. But because the strength increase levels out after 28 days, the two series, M-$SSA_{0sec\ -10\ min}$ and M-$SSAED_{0sec\ -10\ min}$, are roughly compared though taking the difference in the curing time applied into account.

Three prismatic specimens (160mm x 40mm x 40mm) were cast in each mould. After curing they were cut into 6 equal test samples (80mm x 40mm x 40mm). For the determination of the compressive strength a Toni 3000 compression machine was used. The pH was measured and mineralogy investitaged on crused samples for the three different mortars.

The flow value expresses the workability of mortar with untreated and grinded SSA. Preparation of mortars followed DS/EN 191-3+A3 (DS 2009) and the tested mortars are those listed in Table 2. The flow value was determined according to DS/EN 1015-3 (DS 1999). A truncated conical mould (50 mm high, internal diameter 100 mm at the bottom and 70 mm at the top) was uniformly filled with mortar. The mould was removed, and the mortar exposed to jolting by slowly raising the mould 2 cm vertically and dropping it, 15 times at a rate of one pr. second at a flow table. The mean diameter (d_{mean}) from two measurements of the subsequent mortar diameter in two directions at right angles was found. The procedure was repeated twice for each mixture.

For evaluation of the colour differences another type of samples were casted in moulds made from film faced ply wood as desribed in detail in [17]. The dimensions of these moulds were 100x100x30mm. Paper cuttings were used to make both rough and smooth surfaces of the hardened mortar, and a circular shape was cut out of the lining paper using a circle cutter. The paper was moistened under running water for a few seconds. Before the frame was mounted, the wet paper cutting was placed at the base of the mould and evened out with the means of a wall paper brush.

RESULTS AND DISCUSSION

Phosphorous and heavy metals in the SSA before and after ED

The investigated SSA contained 20.6 wt% P_2O_5 (found from the XRF analysis), which corresponds to 9.0 wt% P (Table 3). The P concentration in the investigated ash is slightly lower than in the previously investigated SSA batches from the same facility, 10wt% [10], 12wt% [16] and 11wt% [13], however, the concentration is within the general range (5 – 10 wt% P) reported by Cyr et al. [5].

The initial SSA amount in the experiment was 3 kg, and with a P concentration of 9 wt% the total mass of P was 270 g. During ED, P was extracted from the SSA, and the concentration was decreased to about 1.0 wt% P (2.3 % P_2O_5) in SSA-ED. In ED lab scale experiments from [13] where successful P extraction was obtained from SSA from the same incineration plant, about 50% SSA dissolved, and the same range of dissolution is expected in the present bench-scale experiment. Thus approximately 15 g P was still bound in the SSA after ED, corresponding to 6% of the total.

The concentration of Cd and Cu decreased in the SSA during ED (Table 3). The Cd concentration decreased from 2.8 mg/kg to 0.5 mg/kg (corresponding to 91% removal taking the 50% dissolution of SSA into account) and the Cu concentration decreased from 590 mg/kg to 460 mg/kg (61% removal). This is on the contrary to the concentrations of Pb and Zn, which both increased in the SSA during ED; Pb from 170 to 420 mg/kg and Zn from 2100 to 2600 mg/kg. While the decreased concentrations of Cd and Cu show that they were extracted to a higher extent than the overall ash dissolution, the increased concentrations of Pb and Zn showed that they were extracted to a lesser extent. Taking the SSA dissolution into account, the Pb content was higher in SSA-ED than in the original SSA, which reflect an inhomogeneity in Pb concentration and that the initial sample did not represent the SSA treated by EDR. For Zn, about 38% was removed. The heavy metal mobilization was significantly less than in the lab experiments with SSA from the same plant [13], where 85% Cu, 40% Pb and 77% Zn were mobilized.

Table 3: Characteristics for the experimental materials. * P content in % from the XRF analysis.

	Cement	SSA	SSA-ED	DS/EN-450-1 Requirement
Water content %	0.3	0.3	2.7	
pH	12.6	9.3	3.5	
Water solubility %	-3.6	1.5	1.3	
LOI %				
550˚	0.8	0.5	4.4	Max. 9.0
950˚	7.0	1.6	4.7	
Oxides %				
P_2O_5*	0.2 (0.1*)	20.6 (9*)	2.3 (1*)	-
Al_2O_3	4.9	8.3	6.6	SiO_2+ Al_2O_3+ Fe_2O_3 >70 %
SiO_2	20.1	18.6	39.4	
Fe_2O_3	5.4	15.7	27.3	
SO_3	4.7	19.2	0.3	< 3.0 %
Na_2O	0.7	1.2	0.8	Alkalies < 5 %
K_2O	0.8	1.7	1.8	
MgO	0.5	2.3	1.0	-
MnO	0.04	0.1	0.01	-
CaO	65.8	20.9	1.0	-
TiO_2	0.4	0.9	1.7	-
Cl	0.1	0.02	0.1	Max. 0.1 %

The ED recovery process

As a constant current was applied to the electrodes during the ED experiment, the voltage varied as a result of varying resistivity. The voltage generally decreased between both sets of electrodes, from 30.8 V to about 10 V for Cat-An1 and 30.2 V to 10.8 for Cat-An 2, i.e. the voltage was in the very same range in the two electrode sets. The pH decreased due to the electrolysis at the anodes, and the conductivity of the SSA suspension did subsequently increase. Conductivity and pH in the suspension during the experiment are shown in Fig. 3, and the measurements in the two sampling points (back and front) are varying only very little at every time of analysis.

The experiment can be separated into four zones based on pH: (I) pH decreases from 7 to 3 during over the first approximately 69 hours, (II) pH stabilizes between 2 and 3 until 356 hours, (III) pH decreases gradually to 1 until about 475 hours (approximation as data points were not analysed here), and (IV) pH stabilizes at 1 for the remaining hours of the experiment. The oxidation rate of H_2O at the anode was constant (after 2 days) due to the constant current applied, and thus the rate of H^+ produced was constant. The pH in the suspension is buffered by the SSA in Zone II, and this corresponds to the finding in (Kappel et al. 2017, submitted), where a titration curve showed an ash buffering capacity around pH 2-3. In zone III, this buffering capacity was overcome, at pH decreases. In zone IV it is expected that the current is nearly exclusively carried by H^+ ions, which at this point are present to a very high extent in the suspension. The conductivity of the suspension

is almost linearly increasing over the duration of the experiment irrespectively of pH, showing the release of ions from the SSA during the buffering period in zone II.

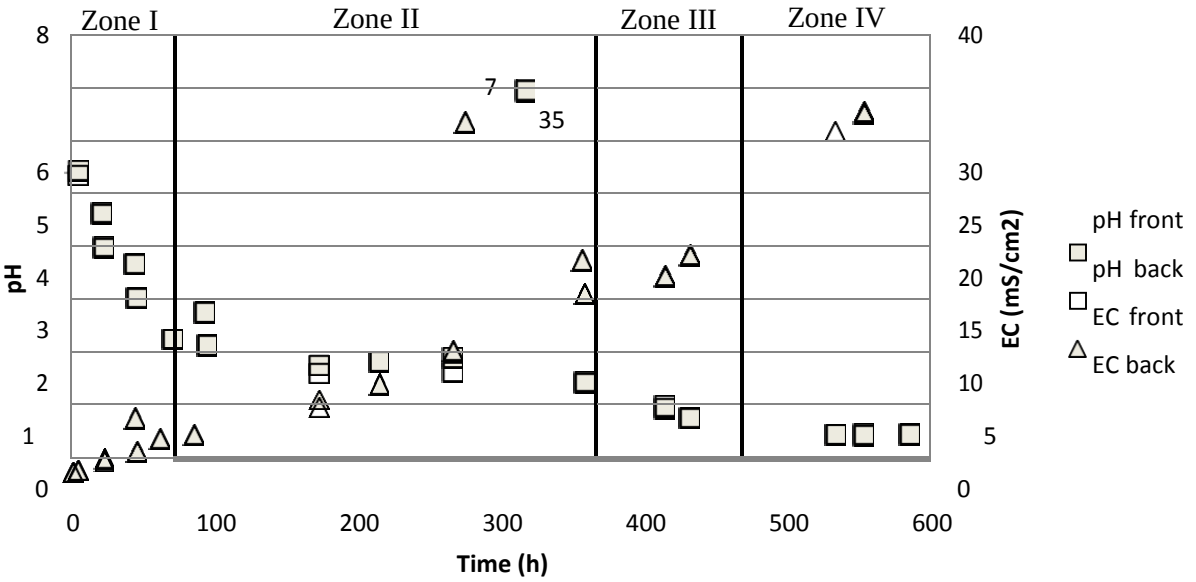

Fig. 3 pH and conductivity on the SSA suspension during the ED experiment

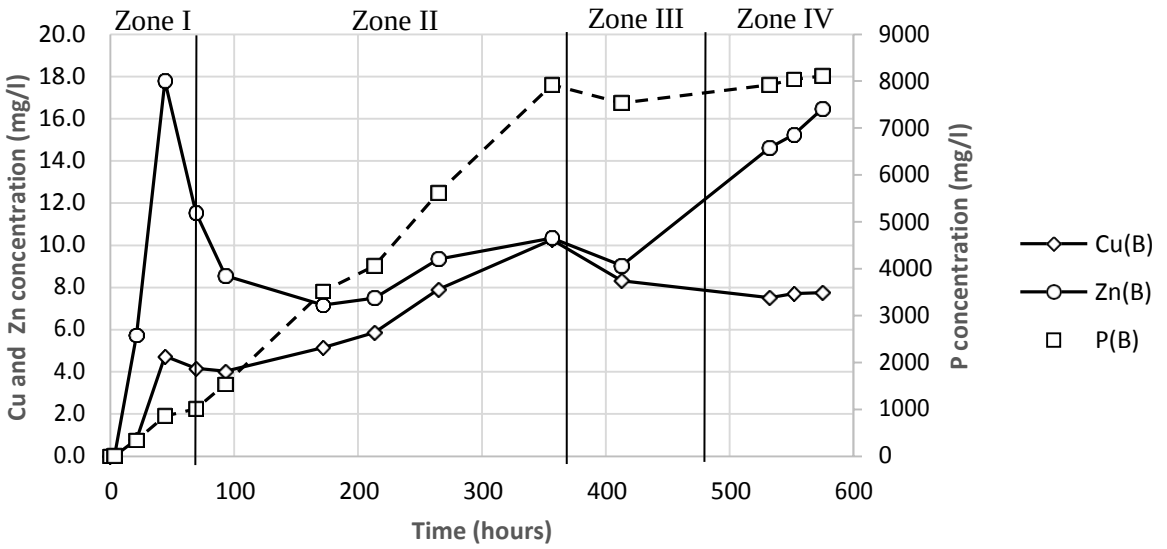

Fig. 4 Concentration of Cu, Zn and P during ED in the liquid of the SSA suspension. The horizontal lines corresponds to the zones in acidification (Fig. 3)

The concentrations of Cu, Zn and P in the filtrate of the SSA suspension during the ED experiments are shown in Fig. 4. Cu represents the heavy metals of which the concentration decreased in the SSA during the treatment and Zn the heavy metals for which the concentration increased.

An almost linear release of P over time is seen during the first two zones, where after the P concentration in the filtrate remains almost constant. Thus the P extraction was finished with Zone

II, and the experiment could have been stopped here after about 360 hours. The P was thus extracted during the period, where the SSA had a buffering capacity around 2-3. It is commonly reported, that SSA contains whitlockite, e.g. [9]. Whitlockite is a group of structurally complex Ca-metal-phosphates, and as whitlockites are acid soluble, these minerals are dissolved during the ED treatment, and may contribute to the buffering capacity in Zone II, however, large amorphous phase in SSA makes the pattern difficult to distinguish. The ED experiment could have been stopped at the end of zone II, as no more P was recovered after this period. The concentration of P was at this point about 8 g/l in the filtrate and with approximately 31 l filtrate this gives about 250 g P totally in the filtrate, which is by far the major part of the P initially in the ash (270 g).

The continuation of the experiment after the maximum extraction of P (zone II) with zone III and IV was not only a waste of energy, but it also decreased the quality of the filtrate as the Zn concentration increased (mainly in zone IV). The separation if heavy metals in this zone are not efficient as the pH is so low, that hydrogen ions will be by far the main charge carrier. Thus it is highly important to stop the ED process at the right time. At the end of zone II, the concentrations of both Cu and Zn were about 10 mg/l, which corresponds to 310 mg. Initially the 3 kg of ash contained 1.8 g Cu and 6.3 g Zn. Thus 18% Cu and 5% Zn was found in the filtrate.

Characteristics of raw and treated ash

Table 3 shows characteristics for the cement, SSA and SSA-ED. The requirements for use of coal fly ash (DS/EN 450-1:2007) in concrete are shown in the table for comparison, to evaluate the general quality of the SSAs. The pH of the SSA decreased from 9.3 to 3.5 during ED. The water solubility was low for both SSAs and should thus not lead to any volume changes when used in mortar. The LoI increase for the cement from 550°C to 950°C is due to the limestone filler in this type of cement and all LoIs met the requirements. The XRF analysis shown as oxides in the materials (Table 3) showed that while the Fe_2O_3 concentration increases the Al_2O_3 concentration decreases during ED. The SiO_2 concentration increases, showing that Si was mainly present in the part of the SSA, which was not dissolved during ED. In SSA-ED the Al_2O_3, Fe_2O_3 and SiO_2 concentrations summed up to 73 % of the mass, whereas in the SSA the sum of these major oxides was 43 %. Comparing these weight percentages to the requirements for coal fly ash used in concrete it was seen that the ED treatment made the SSA more eligible for use in concrete. Also the reduction in SO_3 due to the ED treatment is favourable for the SSA as material. The content of CaO was also greatly reduced in the SSA-ED, which can be linked to the lower pH and that Ca-containing minerals and phases will dissolve at acidic pH. This will also mean that the buffer capacity of the SSA-ED has been reduced and this together with the acidic pH could negatively influence the properties of the mortar when used as substitution for cement.

The heavy metal content and leaching for the cement and SSAs are seen in Table 4 and the concentrations are compared to limit values for reuse of non-hazardous materials for geotechnical purposes [18], as there are no limits for reuse in construction materials. The leaching concentrations of Cu, Pb and Zn in the SSA-ED exceeded these limits, mostly because the SSA after electrodialytic treatment is acidic. Incorporation of ED treated MSWI fly ashes with high leaching concentrations

in mortars have shown comparable leaching levels to a reference mortar for Cd, Cu, Pb and Zn, probably because the metals were incorporated in the alkaline mortar matrix [19]. However, the leaching of the SSA-ED containing mortars should be studied to ensure that there is no unacceptable environmental impact of this use.

Table 4: Heavy metal content in the experimental materials

Heavy metals (mg/kg)	Cement	SSA	SSA-ED	Category 3 [18]
Cd	0.45	2.8	0.5	>0.5
Cu	67.5	590	460	>500
Pb	22	170	420	>40
Zn	115	2100	2600	>500
Heavy metal leaching (µg/l)				
Cd	<20	<20	35	40
Cu	<20	<20	4,730	2,000
Pb	<20	<20	92	70
Zn	<20	<20	48,500	1,500

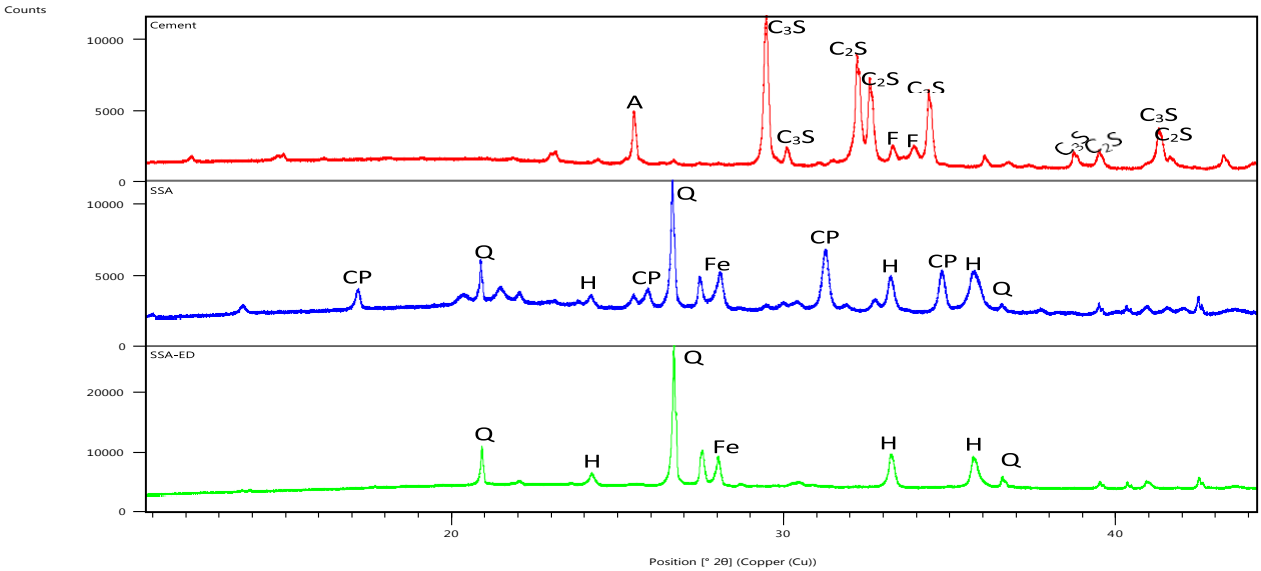

Fig. 5 XRD diffractograms for cement and SSA samples A- anhydrite, Q – quartz, H- hematite, CP- calcium phosphate, Fe – feldspar, C_3S – alite, C_2S – belite, F - ferrite

There were no similarities in the mineralogy between cement and the SSA samples, as seen in Fig. 5. The cement consisted, as expected, of the main cement minerals C_3S (alite), C_2S (belite) and C_4AF (ferrite). Celite (C_3A) was not detected in the diffractogram, which could be due to peak overlap, having the main peak at 33.15 (°2Θ) and ferrite with major peaks at 33.53 (°2Θ) and 33.92 (°2Θ). Rietveld analysis on Portland cement has previously shown 6.5 % C_3A compared to 63.6 % C_3S, 8.9 % C_2S and 14.2 % C_4AF [20]. Anhydrite ($CaSO_4$) was also found in the present cement. The main difference between the raw and ED treated SSA, was the removal of calcium phosphate in

the ED treated ash, which could be expected due to the overall P removal (Table 3). Otherwise SSA and SSA-ED were mineralogically consisting mainly of Q (quartz), Fe (feldspar) and H (hematite).

Mortar properties

The XRD diffractograms for the three different mortars (M-ref, M-SSA and M-SSA-ED the two latter with non-grinded SSA) are seen in Fig. 6. The main mineralogical phases in the mortars were similar regardless of the substitution of cement with SSA. Quartz (SiO_2), the plagioclase feldspars albite ($NaAlSi_3O_8$) and K-spar ($KAlSi_3O_8$), calcite ($CaCO_3$) and the hydration product portlandite ($Ca(OH)_2$) were the main identified minerals. The diffractograms did not show any of the minerals found in the SSAs (Fig. 5). This is likely due to the dominating minerals from the sand, the cement hydration and the dilution effect since SSA only replaced 20 % of the cement. Quartz and feldspars are the most common minerals in sand from Danish sand pits [21] and this is coherent with finding these as the main minerals in the mortars. The pH for all the mortars was 12.3, which shows that the acidic electrodialytic treated SSA did not significantly affect the pH of the mortar on a short term basis.

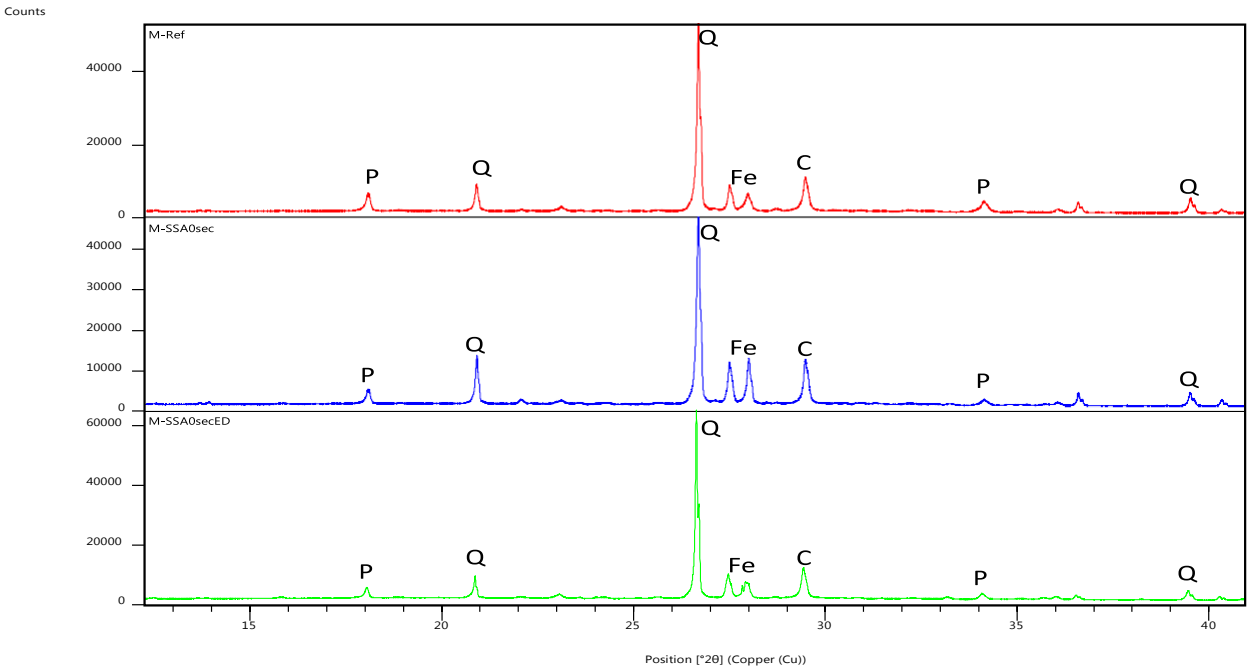

Fig. 6 XRD diffractograms for mortar samples. P- portlandite, Q-quartz, C, calcite, Fe – feldspar

The compressive strength was slightly lower when the mortars contained SSA as well as SSA-ED compared to the reference mortar (Fig. 7a), but the SSA-ED still gave compressive strengths above 50 MPa for all tested mortars, which is sufficient for most uses of concrete. For the mortar with SSA, the compressive strength increased in accordance to an increase in the fineness of the SSA particles (Fig. 7b). This finding corresponds to results reported in the studies of Pan et al., and Donatello et al. [9, 22]. In these two studies, it was found that the specific surface area did not increase significantly even though the fineness of the particles did due to the grinding. Therefore, it was suggested that the SSA particles had a porous structure with many open pores, adding to the

overall specific surface area. As consequence of the high open porosity, the available water in the system was reduced, which could have inhibited the hydration process of the clinker minerals [9] as well as the workability of the mortars [22]. The improved compressive strength (Fig. 7) and workability (Fig. 8) found for M- $SSA_{30\ sec}$ and M-SSA_{10min} supports this assumption. Furthermore, the fineness of a pozzolanic material is important for the hydration process, because fine particles provide extra nucleation sites due to large surface areas and at the same time extra space in the system for hydration products to form and develop at the early stage [23]. In case the fine particles are without pozzolanic activity, they may improve the strength from a filler effect.

Even though the d50 were quite similar for SSA and SSA-ED (Table 1) the graduation differs. The d10 was 14 µm for SSA and 3 µm for SSA-ED, and thus SSA-ED had the largest fraction of the finest particles. At the same time, SSA-ED also had the largest fraction of the coarsest particles, as d90 was 817 µm compared to 356 µm for the SSA. Thus, the grain sizes differed more in SSA-ED than in SSA. After grinding SSA-ED for 30 sec the d90 is still coarser than in the SSA. The increased concentration of Si (Table 3) in SSA-ED, of which a large fraction is present in quarts (Fig. 5) may be related to this. The quarts may originate from the sand in the fluidized bed, i.e. relatively coarse particles, and quarts is not easily grinded to finer particle sizes. Still after 10 min grinding, the SSA-ED has larger d90 than SSA. The increase in compressive strength with increasing fineness found for M-$SSA_{0sec\text{-}10min}$ was not as apparent for M-SSA-$ED_{0sec\text{-}10min}$ due to the larger particle sizes (Fig. 7b). The compressive strength increased from 51 MPa to 55 MPa when grinding the SSA-ED for 30 sec, but the longer grinding (finer particles) did not give further strength increase. This reveals that the grain size graduation obtained with the longer grinding did not improve the packing of particles.

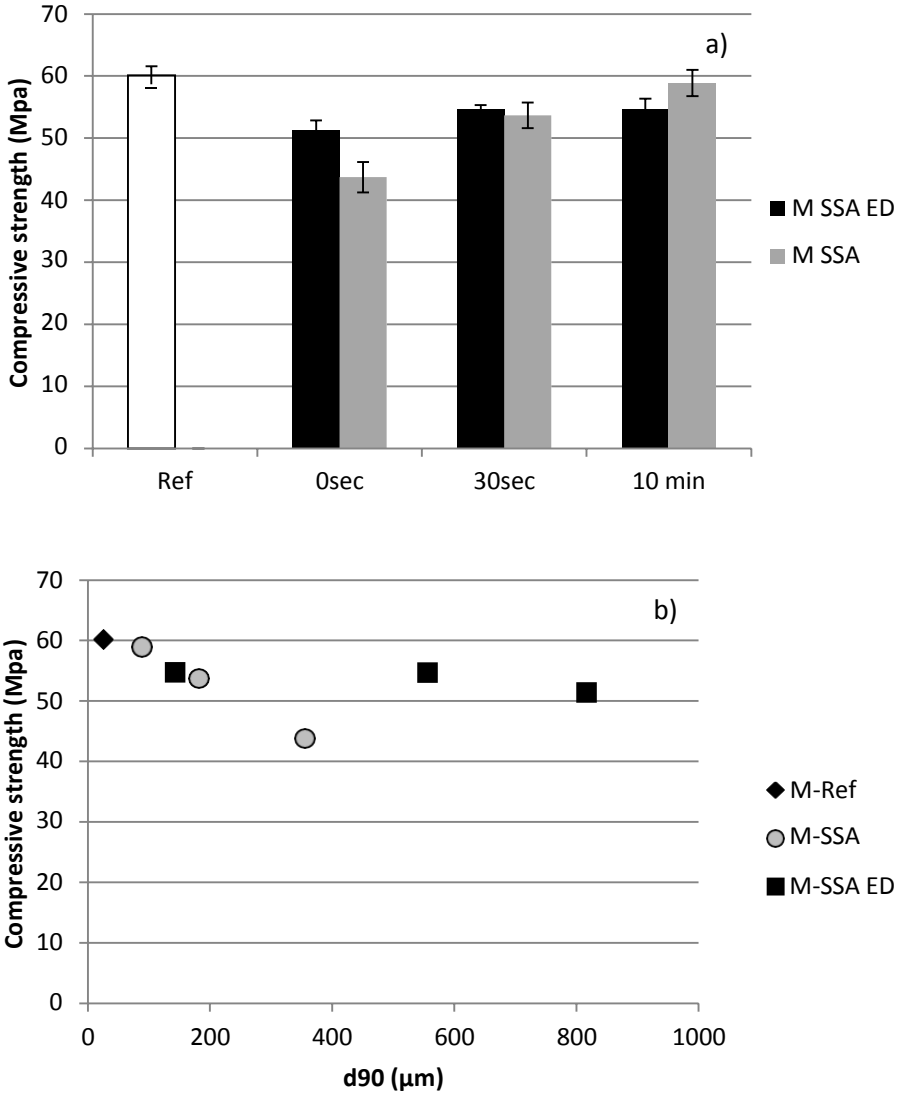

Fig. 7 Compressive strength of the mortars by a) grinding time and b) d90 in the SSA

The workability expressed by flow value spread (Fig. 8) was lower for all mortars with SSA and SSA-ED than for the flow value of the reference mortar. The lower workability was also experienced during the mortar mixing where the SSA mortars were dryer. Increased fineness is generally expected to improve the workability, which was also seen here, especially for the SSA with the grinding time of 10 minutes. The flow value for mortar with grinded SSA increased as expected but smaller particle sizes of SSA-ED$_{30sec\ -10min}$ had no influence on the flow value and did not improve the workability of M-SSAED$_{30sec-10min}$. An irregular morphology of SSA particles is likely adding to a lower workability [24] as well as the porous structure of SSA particles must be expected to influence the workability negatively, in that the pores absorbs water from the mixture [9, 22].

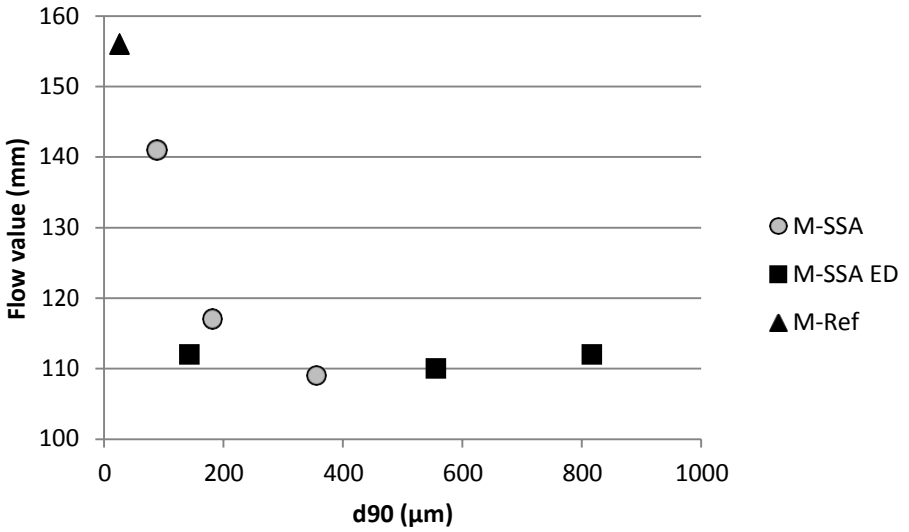

Fig. 8 Workability of the mortars expressed by the flow value spread. The d90 value is for the SSA part of the SSA mortars and for the cement in the reference mortar

Fig. 9 shows the colours of the mortar samples M-SSA$_{0sec-10min}$ and M-SSAED$_{0sec-10min}$.

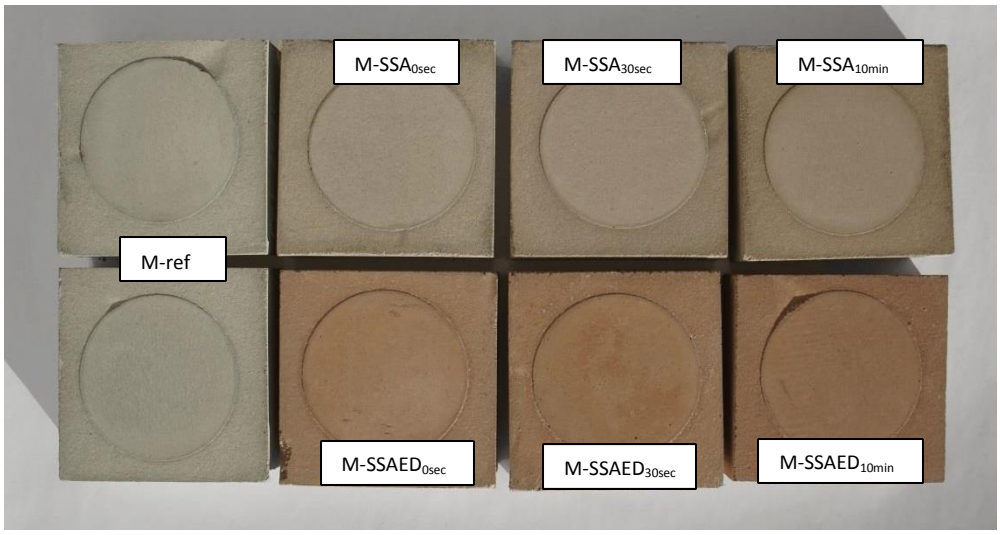

Fig. 9 Colours of the experimental mortars

The three mortars with SSA-ED$_{0sec-10min}$ all had a more intense red colour than the mortars with SSA$_{0sec-10min}$. The colour originates from the hematite (Fe_2O_3, see Fig. 5), and the concentration of Fe was higher in SSA-ED than SSA (Table 3). The saturated red colour was similar for all three samples with SSA-ED$_{0sec-10min}$ whereas the colours of M-SSA$_{0sec-10min}$ evolved slightly in the intensity as the particle size of the SSA decreased. Grinding the ash means larger surface area, which results in the slightly stronger colour of the grinded mortars with SSA. Thus, the colours of M-SSA$_{0sec-10min}$ were induced by the physical changes of the SSA whereas the colours of M-SSAED$_{0sec-10min}$ most likely were due to the chemical changes of SSA-ED. It is possible that a very

low content of CaO together with a higher content of Fe for SSA-ED (Table 3) may have caused the significant colour change of M-SSAED$_{0sec-10min}$ compared to faint colours of M-SSA$_{0sec-10min}$. It is known from the composition of minerals in clay that a high content of Fe together with a low content of CaO generates the red colour known in bricks [25]. The rough and smooth surfaces made by the paper cuttings were made to unfold the aesthetical qualities of the mortar. The rough and smooth surfaces are basic elements of architecture and therefore important for architects and to experience architecture awareness of these elements are necessary [26]. The difference between the smooth parts which are the spherical part of the samples in Fig. 9 and the rough part, accentuate the colours of the mortars. From Fig. 9 it can be seen that the visual difference in the colour tones between rough and smooth parts are clearer for the samples with SSA than for samples with SSAED. The colours of M-SSAED$_{0sec-10min}$ may be conceived as an intrinsic property of the material which aesthetically can be used in the build environment for exposed concrete structures.

CONCLUSION

- Electrodialytic separation extracted 90 % of phosphorous from the SSA. The electrodialytic treatment reduced the pH of the SSA from 9.3 to 3.5, however, no immediate influence of the acidic pH of the ash were seen from the results of the mortar testing. The acidic pH though increased the heavy metal leaching of the electrodialytically treated SSA and the leaching properties should be studied further for the mortars containing the SSA.
- Compressive strengths over 55 MPa were achieved for mortars with SSA, although the compressive strength decreased when replacing cement with SSA compared to the reference (60 MPa).
- The fineness and mineralogy of the SSA changed due to the electrodialytic treatment, probably influenced by the dissolution of the ash constituents at the acidic pH.
- The red color intensified in the mortar with SSA-ED compared to the SSA, into a color similar to red bricks. The red color was homogeneous in the entire mortar sample and on both the smooth and rough surfaces. The study showed that electrodialytic treated SSA may have potentials to be utilized as resource in cement based materials especially in places where the colour aesthetically can add value to the build environment.

Acknowledgements

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5.4 Main research findings

This research has shown that the methods to process SSA: milling, acid washing or electrodialysis, had a significant effect on the basic properties of mortar when SSA was used as partial cement replacement. As such the results of the research cannot determine the feasibility of using SSA as resource in cement based material for a specific use. This requires additional tests and targeted experiments to clarify the long term implications of using SSA as partial cement replacement both technically and environmentally. However, this was not the intention of the research. The intention was to unfold the potential related to the utilisation of SSA as partial cement replacement in cement based materials aesthetically and technically. This was done by documenting how the basic properties of the SSA itself were altered when the SSA was pre-treated, and how ordinary mortar was affected when SSA was processed as a resource and used to replace cement by 20 wt% in mortar. The approach taken in the present research was to address SSA utilisation in the context of solving a resource problem rather than solving a waste problem. This was done by taking into account that SSA is a valuable phosphorous resource before it is as a useful resource for concrete production. This disposition was taken as phosphorous is an irreplaceable nutrient which is regarded as a scarce resource.

5.4.1 The colours of mortar with sewage sludge ash

Selected mortar samples from the three studies conducted are presented coherently embedded in a square consisting of 4x4 samples (Fig 5.3). The mortars with the different SSAs are displayed horizontally in four columns which include from the right two columns with untreated SSA (SSA1 and SSA2) and two columns with phosphorous extracted (SSA2-acid and SSA2-ED). Vertically the duration of the milling increases. The 4 samples in the top row are ordinary mortar which is the point of origin. The collection of samples gives visible evidence of how ordinary mortar responses to the untreated and treated SSA when used as partial cement replacement. What it clearly shows is that the SSA transforms the properties of mortar gradually when the SSA is milled, and instantaneously when phosphorous extracted SSA is used.

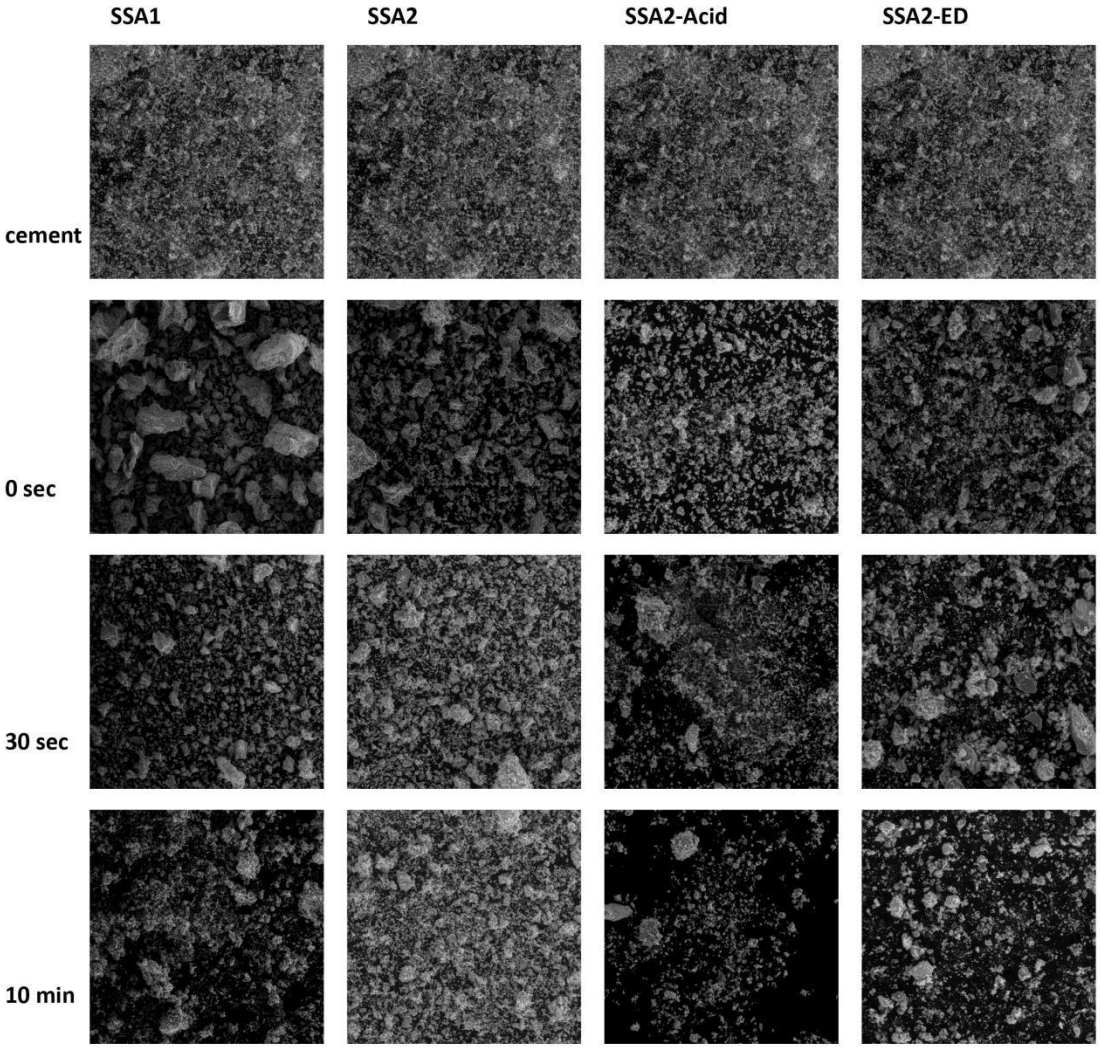

Figure 5.2 SEM images of untreated and treated SSA

Figure 5.3 mortars shown are from left to right: SSA1, SSA2, SSA2-Acid and SSA2-ED

The function of exhibiting the colour samples as a whole was to make potentials of utilising SSA as resource in mortars perceptible for the audience. The samples were made with a sphere-shaped smooth part framed by a rougher part to enhance the experience of the mortar. The qualities of the mortars such as colour and texture are important for a perception of the mortars as sensuous material which also are amongst the elements which an architect " can call into play"(Rasmussen 1962, p.29). Therefore, the collection of samples is an important result of the research because it communicates the aesthetical potentials of mortars with untreated and treated SSA. What it also directly shows is that the colours of the mortars are not one-dimensional but can be elaborated by textural differences of rough and smooth surfaces. The smooth parts reflect the light differently and make the colours seem lighter than the rougher parts. This is particularly visible for the mortar with SSA1 and SSA2 where the sphere shaped smooth part in the centre of the samples are in a lighter colour than the surrounding rougher parts.

Figure 5.4 from left to right SSA1 and SSA2

The samples in the two left columns are the mortars made from two different SSA (SSA1 and SSA2). Both were taken from the same wastewater treatment company Biofos at their facility in Avedøre, Copenhagen, Denmark, but sampled at different times. Both SSA1 and SSA2 had a relatively high content of iron oxide

15.7 % (Table 5.1) which explains the red tones of the two ashes. The colours of SSA1 and SSA2 were slightly different, however. SSA1 had a darker tone whereas SSA2 was in a slightly lighter red orange colour (fig 5.4).

In glaze chemistry it is well established that the colours of glaze are depended on the content of oxides as well as temperatures and the conditions during the glaze firing (Hamer & Hamer 1991; Linnet 1996). Colouring oxides can be divided into two main groups: the alkaline colouring oxides and the amphoteric colouring oxides. The alkaline colouring oxide is self-colouring, which means the colour of the glaze is detectable by the colour of the oxide used (Hamer & Hamer 1991). To this group belong oxides such as MnO, FeO, CuO. Amphoteric coloring oxides do not always produce the same colour, as this depends on the presence of other oxides (Hamer & Hamer 1991). The amphoteric oxides are MnO_2, Fe_2O_3 and Cr_2O_3. It is only the amphoteric colouring oxides, which actually completely can change their colour. Another group of oxides are the alkaline or amphoteric colourless oxides, among these belongs oxides such as ZnO, TiO_2 and Al_2O_3. These colourless oxides can be used for brightening the colour, opacifying or enhancing the transparency of the glazes as well as changing the colours of amphoteric colouring oxides.

Table 5.1 Ash characteristics and major oxide content

	cement	SSA1	SSA2	SSA2-Acid	SSA2-ED
Water%	0.28	0.63	0.31	8.89	2.69
pH	12.6	9.87	9.29	1.94	2.69
Water solubility %		1.27	1.54	16.6	1.27
Major oxides (%)					
Al_2O_3	4.91	5.1	8.31	6.99	6.6
CaO	65.7	23.8	21	3.78	1.0
Fe_2O_3	5.43	15.7	15.7	20	27.3
K_2O	0.81	1.57	1.69	1.93	1.8
MgO	0.53	2.32	2.32	1.18	1.0
MnO	0.04	0.09	0.09	0.01	0.01
Na_2O	0.67	1.15	1.2	2.7	0.8
P_2O_5	0.23	20.2	20.6	2.98	2.3
SiO_2	20.1	17.1	18.6	36.4	39.4
SO_3	4.74	2.02	1.92	0.77	0.3
TiO_2	0.35	0.83	0.88	1.55	1.7
Cl	0.1	0.01	0.02	5.0	0.1

In the case of the SSA1 and SSA2 the content of iron is relatively high because iron salts is used at the wastewater plant to precipitate the phosphorous from the effluent. The colour of Fe_2O_3 ranges from red to black colours, depending on the presence of B_2O_3, Al_2O_3 and TiO_2 (Hamer & Hamer 1991). The high content of iron in SSA1 and SSA2 explains the reddish colours of the two SSAs. The difference in the colours of the two might be related to the content of Al_2O_3 being 3 % higher for SSA2 than SSA1. In glaze chemistry Al is used to alter the red iron oxide colour to a brownish colour (Hamer & Hamer 1991; Linnet 1996). The increased level of Al_2O_3 in SSA2 could explain the colour difference between the two ashes, for which SSA1 has a darker tone of red whereas SSA2 instead was in a red-orange colour.

The difference between the colours of SSA1 and SSA2 is also detectable in the two different series of mortars produced with the ashes (fig 5.3). The colour of the mortar with unmilled SSA1 is less affected than the mortar with unmilled SSA2. For both series the colours intensified as the SSA's were milled, and it became more visible that mortars with SSA1 are slightly more reddish than mortars with SSA2. In figure 5.2 SEM (Scanning Electron Microscopy) images of the morphology of the ashes are shown in accordance to the same experimental frame as the mortar samples shown in figure 5.3. From the images it can be seen that the particles of unmilled SSA1 are larger than the particles of unmilled SSA2, which, due to larger surface area and the distribution of finer particles, could explain why the colour of mortar with unmilled SSA2 is more visible than the colour of mortar with the unmilled SSA. Oppositely, in table 5.2 it shows that 90% (d 90) of SSA2 consists of particles with sizes up to 356 µm (approximately 0.4 mm) against 244 µm for SSA1. However, the smallest fraction d10 is finer for SSA2, which is 14.1 µm against 20.2 µm for SSA1. This might sustain the argument that the distribution of finer particles is the explanation for the difference between the colour tones of the two mortars with unmilled SSA. Even though the particles size distribution of SSA1 and SSA2 seen in table 5.2 cannot confirm what is seen on the images of the morphology in figure 5.2, both sets of results show clearly that the particles sizes decreases when SSA1 and SSA2 are milled which as a consequence provides mortars with increasing red tones. The colours of mortars with untreated SSA is determined by the initial condition of the SSA, and therefore variation in the colours of mortars may

be precondition related to the utilisation of SSA in cement based materials as the content of oxides may vary between different batches, which this research has shown.

Table 5.2 Particle size distributions

	d10 (µm)	d50 (µm)	d90 (µm)
Cement	1.72	8.45	26.2
$SSA1_{0\ sec}$	20.2	97.5	244
$SSA1_{30\ sec}$	4.44	34	127
$SSA1_{10\ min}$	1.68	10.3	59.1
$SSA2_{0\ sec}$	14.1	124	356
$SSA2_{30\ sec}$	5.59	39.8	182
$SSA2_{10\ min}$	3.54	24.1	89.0
$SSA2\text{-}Acid_{0\ sec}$	7.64	101	1085
$SSA2\text{-}Acid_{30\ sec}$	5.59	39.8	182
$SSA2\text{-}Acid_{10\ min}$	2.91	18.8	122
$SSA2\text{-}ED_{0\ sec}$	2.79	101	817
$SSA2\text{-}ED_{30\ sec}$	2.22	44.1	556
$SSA2\text{-}ED_{10\ min}$	1.34	9.50	142

The impact of the acid washing and electrodialytic treatment of the SSA2 (SSA2-acid and SSA2-ED) had a significant influence on the colour of the mortar as the colours changed into two different shades of red. The colours of the mortars in the two series were saturated and did not evolve noticeable when the treated SSA2s were milled (fig 5.3). Some of the main differences between the raw SSA2 and SSA2-Acid and SSA2- ED are the pH, the content of CaO, Fe_2O_3 , SiO_2 and P_2O_5, and for SSA2-Acid also the water solubility and the content of Cl. There is a slight difference between the colours of untreated SSA2 and the two phosphorous extracted SSA2-Acid and SSA2-ED (fig 5.5). SSA2-Acid is in darker red tone than the original SSA2 and electrodialytically treated SSA2-ED. However, the difference of the colours in the mortar is more distinct than the colours of the two treated ashes: SSA2-acid and SSA2-ED. The level of iron is higher in SSA2-ED than the level found in SSA2-Acid (table 5.1). This might explain some of the reason why the colours of mortars with SSA2-ED are more intense and in a darker tone than the series with SSA2-Acid

Figure 5.5 left to right: SSA2, SSA2-Acid and SSA2-ED

The significant different colours in the mortars containing these phosphorous extracted SSAs could also be due to the decomposition of chemical compounds and changes of the mineralogy of SSA2-Acid and SSA2-ED. The major mineral phases of the different SSAs are detected by the XRD diffractograms (figure 5.6). The mineralogy shows that calcium phosphate (CP) is the main phosphate mineral in SSA1 and SSA2, and that phosphate minerals are not present in SSA2-Acid or SSA2-ED. Instead, only hematite (H), quartz (Q) and fledspar (Fe) can be detected in the two phosphorous extracted SSAs. An increase of iron, the much lower concentration of phosphorous, removal of calcium and the decomposition of the mineral structure of the SSA2 due to the extraction of phosphorous may have been the causes for the intensified colouration of the mortars with SSA2-Acid and SSA2-ED. Both phosphorous and calcium can supress the colour of amphoteric F_2O_5 which is a mechanism known from glaze chemistry (Linnet 1996) In regards to SSA2-Acid, the high content of chloride from the HCl, which was used to extract phosphorous, could have caused the formation of other iron complexes with chloride, such as anionic ferric chloride complexes (Nakanishi et al. 2002), which in a solution can have generated the saturated reddish colour, significantly different from the colour of mortar with untreated SSA2.

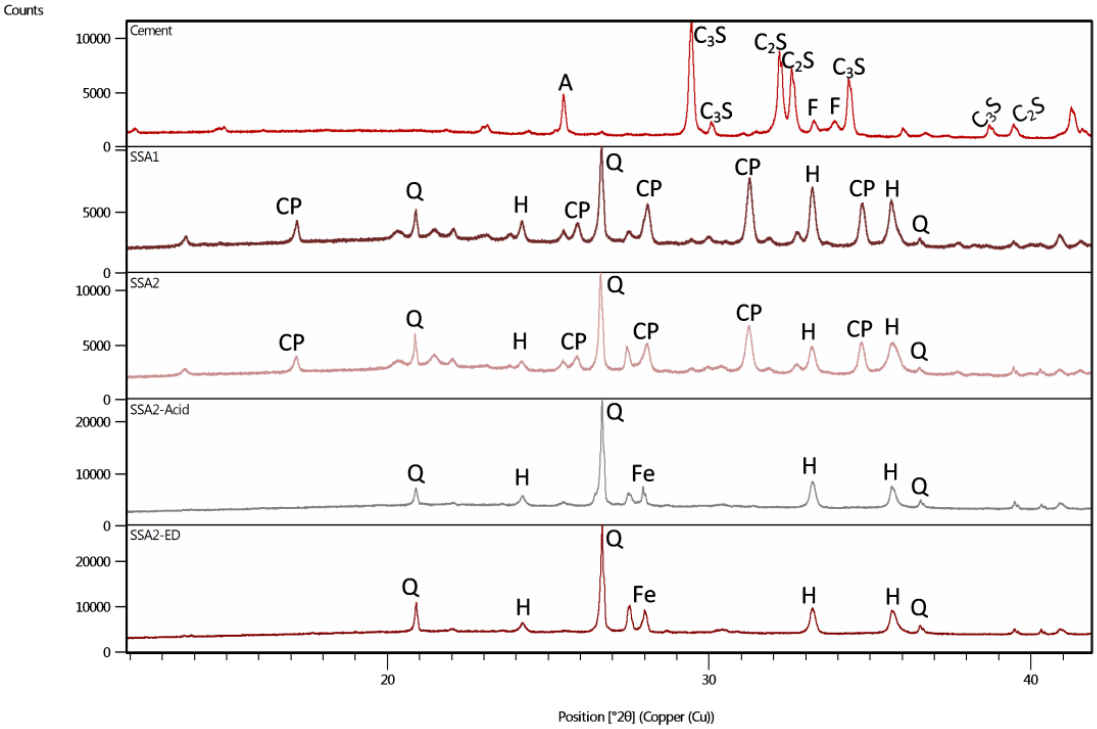

Figure 5.6 XRD diffractograms for cement and SSA samples A- anhydrite, Q – quartz, H- hematite, CP- calcium phosphate, Fe – feldspar, C3S – alite, C2S – belite, F - ferrite

5.4.2. The Influence of sewage sludge ash SSA on compressive strength and workability

The compressive strength of the mortars are shown in figure 5.8, the flow value in figure 5.9 and the grain size distribution of the SSAs in table 5.2. The compressive strength for mortars with untreated SSA1 was higher than mortars with SSA2, however, the compressive strength increased to an extent where it reached the strength of ordinary mortar when SSA1 and SSA2 were milled. The flow value was lower for the mortar with unmilled SSA1 in comparison to the flow value found for mortar with unmilled SSA2. But the flow value increased instantly when SSA1 was milled 30sec -10 min, however, without reaching the flow value of ordinary mortar. The flow value and the compressive strength development also improved for mortars with milled SSA2, but not to the same extend as the flow value and the compressive strength of ordinary mortar or mortar with milled SSA1.

Previous studies by Pan et al. (2003) and Donatello et al. (2010a) have, similarly to the results of present research, found that the milling of SSA has a positive impact on the strength development and the flow value of mortars with SSA. In the experiments of the present research the water/cement ratio was kept constant in the mix design of the different test mortars. Thus, from the results it can be seen that the improvement of the workability expressed by the flow value and the compressive strength development are two parameters correlating. There could be several reasons for the increase of compressive strength, however, the fineness of particle sizes is evidently important as the compressive strength and the flow value increased when the fineness of the SSA increased due to the milling (table 5.2). Another important parameter could be the alteration of morphology of the SSA. The SEM images seen in figure 5.2 show the morphology of the unmilled SSA1 and SSA2 as coarse, angular and large particles especially in comparison to the particles of the powdery cement. In the studies of Pan et al. (2003) and Donatello et al. (2010a) the influence of milling SSA on properties of SSA and the strength development were discussed. The two studies measured the specific surface area and found it didn't increase significantly when the fineness of the particles increased. An explanation to this was found to be related to the morphology of the SSA, which not only was characterised by the coarse and irregular particles but also by having many open pores. The open pores of SSA may suck and trap water and as result lower the free water in the system. Furthermore, the shape of the particles can affect the internal friction in fresh mortar when particles are as SSA coarse and irregular. Therefore if the shapes of the particles are rounded the internal friction is reduced (Pan et al. 2003). As a consequence the workability is improved and with that also the compressive strength. For mortars with treated SSA; SSA2-Acid and SSA2-ED, the milling of the SSAs did not have the same influence on the compressive strength as it did for mortar with SSA1 or SSA2. The initial compressive strength of the mortar with SSA2-Acid was high and comparable to the strength of ordinary mortar (fig 5.8). The compressive strength did not increase significantly when the SSA2-Acid was milled. The initial compressive strength found for mortar with unmilled SSA2-ED was approximately 8 % less than the compressive strength of ordinary mortar. The fresh mortar with unmilled SSA2-ED and SSA2-Acid were both very dry and the flow values were close to zero, as the initial diameter of the sample only increased by approximately one centimetre during the run of the experiment monitoring the flow value of the test mortars (fig 5.9).

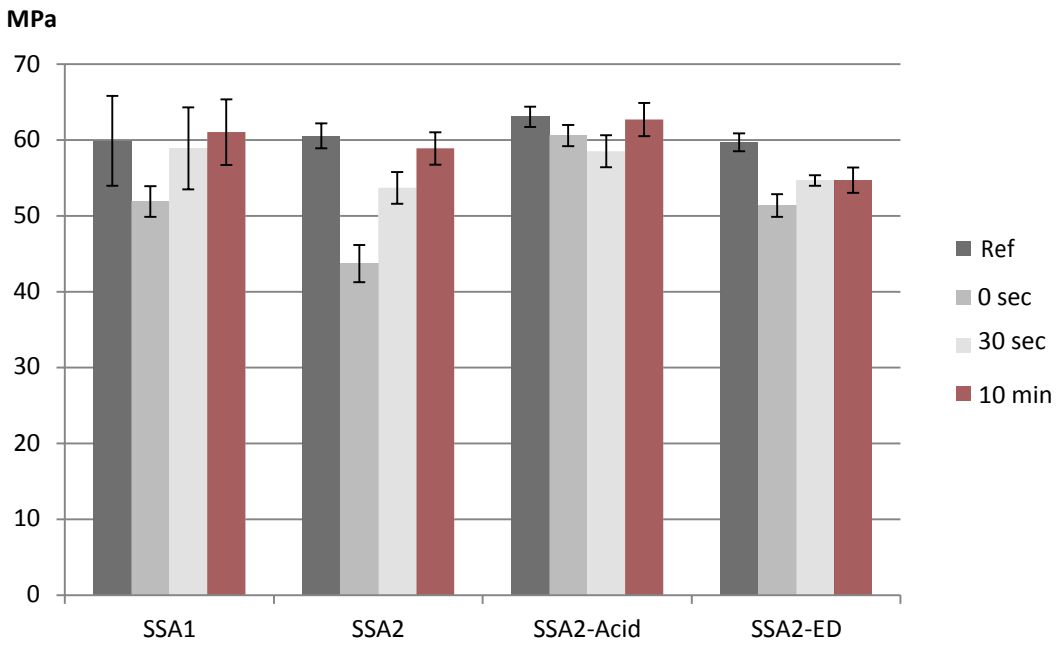

Figure 5.8 The compressive strength of the mortars after 28 days

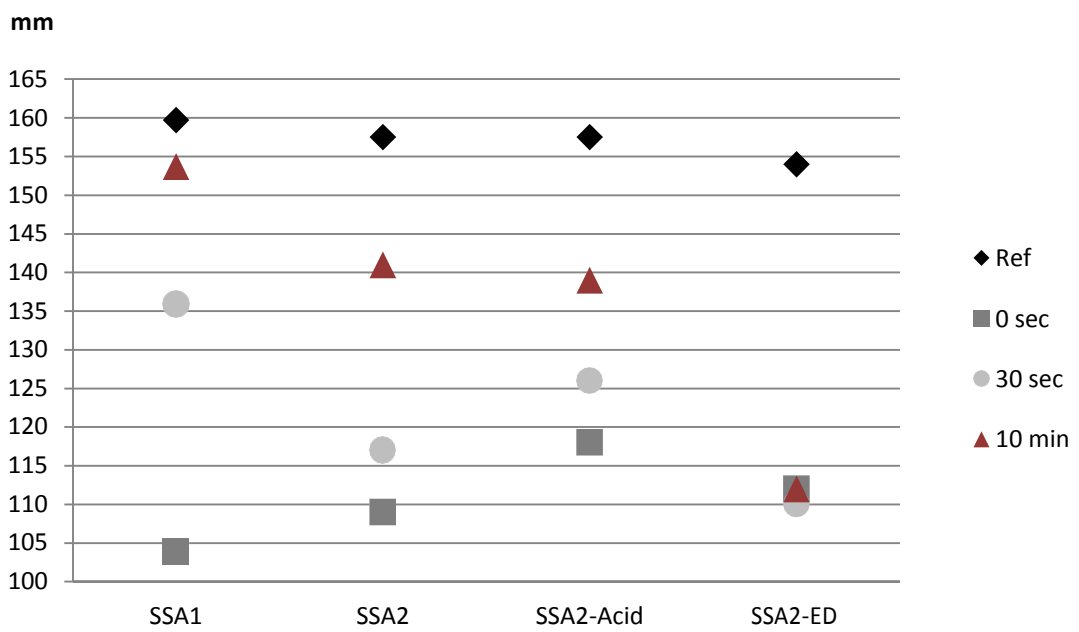

Figure 5.9 The flow value of the fresh mortars

Figure 5.9 also shows that the milling of the SSA2-ED did not have any effect on the workability of the mortars, as the flow value did not increase when the SSA2-ED was milled. For mortar with SSA2-Acid the milling improved the workability as the flow value increased gradually as the particle sizes decreased, and eventually reached the flow value of mortar with untreated SSA2 milled for 10 min. The milling of the SSA2 –ED was not the main parameter affecting the properties of mortar, and the milling of SSA2-Acid had only impact on the flow values of the mortars with SSA2-Acid. Thus, a correlation between an improved compressive strength and workability due to alteration of the morphology of SSA2-Acid and SSA2-ED were not seen for mortars with treated SSA.

As for the colours of the mortars with either SSA2-Acid and SSA2-ED the chemical change and consequently the change in mineralogy of the two treated SSAs (fig 5.7) were the main parameters influencing the compressive strength developments, and for mortars with SSA2-ED also the flow value. The oxides, which were removed in SSA2-Acid and SSA2-ED, were mainly CaO and P_2O_5 and oxides with increased concentrations were $SiO_{2,}$, Fe_2O_5. For the acid washed SSA content of Cl and water solubility were quite high (table 5.1), and for both ashes the originally alkaline SSA2 was acidified due to the treatments. The initial strength of mortars in both series with treated SSA2 (unmilled SSA2-acid and SSA2-ED) was higher in comparison to the initial compressive strength of mortar with only unmilled SSA2, even though the particles of unmilled SSA2-Acid and SSA2-ED were larger than the particles of unmilled SSA2. This confirms that the chemical changes prompted the reactivity of mortars and improved compressive strength and for mortars with SSA2-Acid also the workability.

5.4.3. Environmental considerations

One of the main concerns related to the use of acid washed and electrodialytic treated SSA as partial cement replacement is the fact that the leaching of the heavy metals increases when the pH of SSA2-Acid and SSA2- ED decreases (table 5.1).

Table 5.3 Ash characterisation

Elements mg/kg	cement	SSA1	SSA2	SSA2-Acid	SSA2-ED
Al	18600 ± 3850	22500 ± 298	32000 ± 678	17700 ± 465	15000 ± 586
As	10.8 ± 2.67	10.1 ± 0.39	9.59 ± 1.05	0.42 ± 0.47	6.06 ± 0.31
Ba	240 ± 45	674 ± 0.39	724 ± 23.3	1410 ± 25.9	1660 ± 65.6
Ca	360000 ± 81200	149000 ± 1470	124000 ± 3980	17400 ± 389	3720 ± 102
Cd	0.45 ± 0.16	2.63 ± 0.16	2.77 ± 0.08	0.43 ± 0.04	0.50 ± 0.03
Cr	26 ± 4.85	38.7 ± 0.76	40.2 ± 1.17	61.3 ± 1.38	64.4 ± 1.79
Cr IV[i]	3.6		0.5	2.4	
Cu	67.5 ± 13.1	668 ± 17.3	590 ± 20.4	359 ± 11.4	464 ± 14.8
Fe	16900 ± 3210	57200 ± 1430	74300 ± 1300	76800 ± 2490	83300 ± 3240
K	2650 ± 575	5640 ± 50.1	6140 ± 153	4130 ± 58.8	3130 ±87.7
Hg[i]	0.4	n.d*	4.33	7.73	n.d*
Mg	2840 ±529	17000 ± 378	16000 ± 371	4150 ± 103	3240 ± 83.5
Mn	127 ± 24.1	710 ± 7.95	688 ± 12.9	285 ± 6.71	252 ±7.21
Na	1210 ±231	3930 ± 51.5	3440 ± 104	1480 ± 50.6	1450 ± 46.4
Ni	27 ± 5.55	57.5 ± 1.53	60.9 ± 1.8	71.7 ± 1.36	96.4 ± 2.66
P	876 ± 167	130000 ± 2014	126000 ± 3140	14400 ± 266	13100 ± 842
Pb	22 ± 4.89	144 ± 2.00	172 ± 4.89	234 ± 7.67	423 ± 1.54
Se	4.54 ± 1.97	n.d	6.16 ± 3.15	7.31 ± 1.35	1.54 ± 0.84
Zn	115 ±22	1930 ± 26.8	2100 ± 52.8	1890 ± 52.9	2603 ± 115
Leachings ug/l					
Cl	130000 ± 5500	13400 ± 89.1	23300 ± 437	23900000 ± 309000	510000 ± 8350
SO4	21400 ± 3990	1220000 ± 5240	2520000 ± 78700	2610000 ± 137000	943000 ± 21000
Na	707000 ± 15700	182000 ± 1680	210000 ± 6610	375000 ± 9340	89000 ± 2270
Al	590 ± 772	99.7 ± 74.3	527 ± 322	140000 ± 44900	10000 ± 694
As	<20**	8.84 ± 3.42	21.7 ± 1.48	<20**	64.8 ± 1.52
Ba	11300 ± 235	548 ± 344	1020 ± 1237	1360 ± 13.1	144 ± 26.8
Ca	545000 ± 19100	732000 ± 6630	637000 ± 18500	6490000 ± 261000	1050000 ± 19700
Cd	<20**	<20**	<20**	178 ± 0.62	35.2 ± 0.02
Cr	40.9 ± 1.8	0.44 ± 0.76	0.18 ± 0.32	135 ± 1.31	47.5 ± 1.60
Cu	7.28 ± 1.05	3.78 ± 1.10	4.43 ± 0.89	78300 ± 696	4730 ± 179
Fe	<2000**	<2000**	<2000**	26700 ± 361	749 ±104
K	1480000 ± 24400	137000 ± 54.8	145000 ± 3380	848000 ± 24900	22700 ± 259
Hg[i]	<1**	n.d*	<1**	128	n.d*
Mg	<2000*	29100 ± 991	187000 ± 4380	1110000 ± 11542	244000 ± 5360
Mn	<20**	<20**	9.57 ± 4.15	63100 ± 422	9500 ± 242
Ni	0.82 ± 0.71	<20**	<20**	6690 ± 8.89	2920 ± 29.8
P	<2000**	<2000**	<2000**	39500 ± 312	563000 ± 13600
Pb	<20**	<20*	<20**	273 ± 6.99	91.9 ± 11.0
Se	38.3 ± 9.15	n.d*	507 ± 6.47	26.9 ± 16.7	129 ± 11.8
Zn	<20**	<20**	<20**	319000 ± 10500	48500 ± 794

*Not determined **below standard

In table 5.3 the concentration levels of heavy metals and leaching from untreated and treated SSA are listed. They are assessed by comparing the concentration levels of heavy metals and leachings with Danish limit values included in the legislation known as *"Restproduktbekendtgørelsen"* (Miljø- og fødevareministeriet 2016) set for non-hazardous construction waste, soil and residues reused in geotechnical constructions. These limits are used to assess the SSAs here, as there are no limiting values related directly to SCM. The target elements included in *"Restproduktbekendtgørelsen"* are in table 5.3 marked grey. The elements marked light pink allows for the waste or residue to be reused however, with restrictions. Elements marked dark pink are exceeding the limit values and it is therefore not allowed to use the waste and residue exceeding.

None of the tested materials comply with the limit values in *"Restproduktbekendtgørelsen*", and surprisingly cement exceeds the limit value in the leaching of Ba, and has a relatively high leaching of Cr and Se. The results in the table also show that in SSA2 Ni, Pb Zn and Hg, are the elements of concern as these exceed the total concentration levels accepted in *"Restproduktbekendtgørelsen"*. In the treated SSA2-Acid and SSA2-ED the same elements are found to exceed the accepted limit values. However, the number of elements does not increase due to the acid washing or electrodialysis. Oppositely the heavy metals exceeding the limit values set for the leaching increase significantly when the SSA2 is either acid washed or electrodialytically treated.

In overall the total metal concentrations in SSA2-Acid was lower than in SSA2-ED, but the metal leaching was generally higher in SSA2-Acid. This is linked to the lower pH in the SSA2-Acid (1.94) compared to the pH of SSA-ED (2.69), as the metal availability is highly pH dependent in SSA (Ottosen et al, 2013, Guedes et al. 2016). The studies conducted in regards to extracting the phosphorous focused only one main aspect, which was to produce sufficient amount phosphorous extracted SSA. The success criterion for experiments was to meet the goal as formulated in the National Danish strategy "Denmark without waste", which was to be able to recycle 80 % of phosphorous from sludge. In the two studies in which phosphorous was extracted either by hydrochloric acid or electrodialysis the criterion was successfully met. However, both methods used are not fully developed and research is still undergoing. Research in extraction of phosphorous from SSA by electrodialysis have shown that tools to stabilize the acidified SSA are available by increasing pH so

that SSA becomes alkaline by which most heavy metals are immobile (Viader 2016). This method may solve the leaching problem related to electrodialytically treated SSA. In the case of SSA2-acid the water solubility was quite high 16.6 % and the additional removal of chlorides compounds may further reduce the leaching and content of heavy metals.

6 CONCLUSION

Utilisation of SSA as resource in production of cement based materials may challenge the conception of concrete as a homogenous construction material commonly associated with the grey colour. First of all, the colour of mortars with SSA can vary and intensify in accordance to the properties of untreated SSA, the amount and methods used to process the SSA before used in cement based materials.

Milling of the SSA was found necessary in order to see any significant colour change on mortars with one of the batches of untreated SSA (SSA1). However, this was not seen for the mortar containing the second batch even though SSA2 was collected from the same wastewater treatment plant. Therefore, variation in the colours between batches as found in the results of present research shows that the colours of SSA in general can vary in accordance to e.g. the conditions of the sludge, its thermal history and consequently the character and the content of oxides. The milled iron rich SSA can provide colours ranging from grey to different red tones, and therefore the process of milling the SSA has the potential to alter the grey colour of ordinary mortar into several tones of red. Treatments to extract phosphorous significantly changes the colours of mortars into saturated red tones, and therefore when phosphorous is recovered from the SSA, the visual appearance of the mortars moves away from the visual appearance of ordinary mortar. This fundamental transformation of the mortars, in which phosphorous extracted SSA is used as partial cement replacement, may also broaden the aesthetical interpretations of cement based materials in the build environment.

The gradual change of the colour found for mortar with untreated SSA (SSA1 and SSA2) did not follow when the acid washed and electrodialytic treated SSA was milled. Instead the mortars changed noticeable when the SSA was processed either by acid washing or electrodialytic treatment for recovery of phosphorous, and thereafter utilised as partial cement replacement in mortar. Consequently, the grey colour of ordinary mortar was instantly overtaken by two shades of red depending on the phosphorous extraction method used. The colour of the SSAs and mortars were found to be caused by Fe_2O_3 that gives a red colour. Due to the acid washing and electrodialytic treatment of the SSA the mineralogy changed. Calcium phosphate was removed; the content of iron increased and for the acid washed SSA also the content of

chlorides. The distinct colours of mortars with acidified SSA where likely influenced by factors mentioned above e.g by the removal of calcium and phosphorous, which supresses the colour of amphoteric Fe_2O_3.

The tendency for the compressive strength development and workability of mortars with milled, untreated SSA was improved performance when the milling duration (i.e. particle fineness) increased. With increased milling duration the performance got closer to the performance of ordinary mortar. Therefore, compressive strength development and the flow value of mortars with untreated SSA are highly determined by particle size distribution. For mortars with acid washed and electrodialytic treated SSA, the dominating parameter influencing the performance of the mortars was chemically induced. Only the workability of mortar with acid washed SSA was altered by milling the treated SSA. Initially, the compressive strength was higher than mortar with untreated SSA, and for mortar with acid washed SSA the strength was comparable to ordinary mortar. In regards to the workability of the fresh mortars with the phosphorous extracted SSAs, the mixtures were dry and therefore not very workable, and as mentioned it was only mortar with acid washed SSA, which benefitted from the milling. The workability of the mortar is an important property for the usage of the material in construction and in fabrication of concrete components. Therefore, further investigations are needed to specify the limitation or possibilities to utilise electrodialytic treated SSA as partial cement replacement. For the utilisation of mortar with acid washed SSA the main concern is related to the content of Cl, which was high compared to the electrodialytic treated and the untreated SSA. Chlorides are deleterious to steel as it will corrode when exposed to high concentration of chlorides in moist and oxic conditions. Therefore, these levels need to be decreased if the acid washed SSA are to be used for reinforced concrete.

Concerns related to the utilisation of the acid washed and the electrodialytic treated SSA are the environmental and hazardous risks of the acidified SSA. Incineration of sludge is used as a waste handling option with the benefits of not only reducing the volume of the sludge but also to prevent pathogens to spread and the stabilisation of containments present in the sludge. The concentration of heavy metals increases when sludge is incinerated, but the heavy metals are mainly bound in stable complexes. This was

shown in the results on the leaching of the problematic elements such as Pb, Zn and Hg. The leaching of these elements was low even though the concentration levels were relatively high in the untreated SSA compared to limit values of Restproduktbekendtgørelsen. Due to acidification of the phosphorous extracted SSA by the acid washing and electrodialytic treatment, the majority of heavy metals detected were mobilised. The results of the present research showed that the hazardous risk increases when phosphorous is extracted either by acid washing or electrodialytic treatment compared to the untreated SSA, because of the pH decrease and the transition of SSA2 from alkaline to acidic. Further development of methods to stabilise the acidified SSA is suggested to ensure safe use and application in the build environment.

In conclusion, the fact that SSA is valuable source for phosphorous before it is a waste material useful as partial cement replacement in mortar and concrete, also establishes the potentials and constrains of its utilisation in cement based materials. The result of present research shows that it is possible to produce mortars with phosphorous extracted SSA, which are distinct from ordinary mortar. The performance of mortars with treated SSA may challenge the practicability of using the materials, as the mortars are significantly different from both mortar with untreated SSA and ordinary mortar. However, the research shows that the potentials are conditioned by the circumstance that the SSA first and foremost was regarded as source for phosphorous, especially the changing colours of the mortars, as these also may broaden the perception of cement based materials normally associated to the grey colour.

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Research in sewage sludge ash (SSA) in concrete has mainly been focusing on SSA as partial cement replacement without taking into consideration that SSA is valuable source for phosphorous (P). In present research two methods to extract P were used, and the overall question of interest was how P extracted SSA affected basic properties of mortar when used as partial cement replacement. The aim of the research was to provide a common ground relevant for different disciplines of Civil Engineering and Architecture to discuss aesthetical and technical potentials of concrete with P extracted SSA

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