



Sewage Sludge Ash used as Supplementary Cementitious Material in Mortar and its Effects on Hygrothermal Parameters and Indoor Environment Quality in Buildings

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Sewage Sludge Ash used as Supplementary Cementitious Material in Mortar and its Effects on Hygrothermal Parameters and Indoor Environment Quality in Buildings

Barbora Krejčíříková

Ph.D. Thesis

Department of Civil Engineering
Technical University of Denmark

2020

Figure front page:

Photo of two sewage sludge ashes (Avedøre grinded and water washed, Lynetten grinded and water washed) and cement in the glass containers.

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*“Be part of the solution,
not part of the pollution”*
(--Unknown)

Preface

This thesis is submitted as a partial fulfilment of the requirements for the Danish Ph.D. degree. The thesis is based on experimental investigations and subsequent analytical data processing carried out as a subproject of the ZeroWaste initiative intending to develop new construction materials based on increased replacement of material constituents with secondary resources such as recycled materials at the end of life cycle. The project was undertaken at the Department of Civil Engineering at the Technical University of Denmark, Kgs. Lyngby, Denmark between January 2013 and July 2017.

The project included an external research stay at the Syracuse University, USA for 7 months and a leave of absence for 13 months due to maternity leave.

The principal supervisor of the Ph.D. project was Professor Carsten Rode from DTU Civil Engineering with co-supervisors Associate Professor Pawel Wargocki, Associate Professor Jakub Kolarik, both from DTU Civil Engineering and Research Director Ruut Peuhkuri from Department of the Built Environment, Aalborg University.

Kgs. Lyngby, August 2020



Barbora Krejčířiková

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The present work would not have been achieved without the help and support of a group of people and hereby I would like to take the opportunity to express my sincere gratitude.

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we have never met in person, we spent numerous hours on Skype discussing both experimental and simulation outcome that resulted in our common conference paper. I would like to express my sincere gratitude for his enormous help, kindness and patience he paid me.

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If by any chance I missed out someone here, be sure you are not forgotten and I sincerely appreciate your help and support: Let this line serve as my gratitude.

Thank you!

Abstract

The overexploitation of available natural resources and its possible adverse effects on environment are prevailing and extensive problems faced by the construction industry. Specifically, cement is the second most consumed substance by weight in the world, after water, and during its production 900 kg of CO₂ are emitted per ton of cement. The growing demand for reduced emissions of CO₂ urges the cement industry to find materials with low CO₂ footprint, which calls for cement substitution. In order to achieve feasible rates of cement substitution, it is necessary to introduce new supplementary cementitious material (SCM), which is readily and possibly locally available. Sewage sludge ash (SSA) could be such a viable resource. An assumption of the study has been that SSA, as an industrial by-product, can be applied as a potential cement substitute in cement-based materials without compromising the material performance. In order to corroborate or disprove this assumption, various material examinations were performed together with different methodologies of material characterization.

The Ph.D. study investigated partial replacement of cement by SSA in mortar and its effect on hygrothermal properties of mortar and impact on indoor air quality. An overall scope of the study was to examine how mortars of different composition interact with the indoor climate. Additionally, the aim was to compare methods applied when assessing hygroscopic performance of cementitious materials and their impact on indoor air quality. This calls for a cross-disciplinary approach.

Three main research tasks were carried out in order to meet the goals: (1) Ash characterization and investigation of the effect of cement substitution on selected physical properties of mortar. (2) Examination of the effect of ash content on hygrothermal characteristics of mortar. (3) Sensory and chemical measurements of mortar emissions and interaction of mortar with typical indoor pollutants.

Two SSAs were used as a substitute for cement in the study. They originated from two major Danish incineration plants located in Avedøre and Lynetten in the Greater Copenhagen area. The effects of different ratios of cement substitution in mortar and two pre-treatment methods of ashes were investigated.

First of all, the results on characterization of SSAs confirmed previous findings concluding that chemical composition of SSAs is highly variable and even their origin from wastewater treatment plants located in the nearby areas does not ensure comparable quality. Moreover, granulometric examination showed that the SSAs typically consisted of larger particles compared to cement particles. Incorporation of ash in cement-ash-based mortar resulted in more porous mortar structures compared to cement-based mortar, which adversely affected the mechanical properties of mortar such as the compressive strength. The hygroscopic sorption properties of the individual constituents alone and of complete mortar samples were described by sorption isotherms for water

vapour and by a capillary water absorption test. Although the sorption abilities of individual constituents were significantly different, the effect of ash content on the sorption isotherms of cement-ash-based mortars was minor. The water absorption coefficient of mortar samples increased significantly with the ash to cement ratio. This indicates that the higher porosity of cement-ash-based mortars have more pores in the capillary range than cement-based mortars.

Hygrothermal properties of the cement-based mortar and cement-ash-based mortar were examined by means of various tests, specifically: thermal conductivity, two hygroscopic sorption tests and water vapour permeability measurements. The measurements showed that the higher porosity of mortar was responsible for a decrease of thermal conductivity and an increase of vapour permeability of mortar. This was expected as these are a function of porosity. Sorption was tested by two methods: the climatic chamber method and the desiccator method. The observations proved that the sorption isotherms were influenced by the method applied, i.e. CO₂ concentration in the supplied air. The method using sealed glass vessels as desiccators showed minor or no differences between cement-based and cement-ash-based mortar, while differences were observed between different mortar mixtures when the climatic chamber method was applied with its atmospheric CO₂ content. Comparison of both methods revealed that the method applied may affect measured parameters to such an extent that the reported results may differ. The assessment of hygroscopic properties of cementitious materials is not clearly defined in any standard and is not easy to evaluate considering that it can be easily affected by various factors. There is a need to delineate standard methodology for hygrothermal assessment of cementitious materials.

Additionally, test on presence of calcium carbonate (CaCO₃) content was performed to detect the effect of carbonation on mortar samples. CaCO₃ was detected in all the mortar samples. With respect to mortar composition, CaCO₃ content was higher for cement-based mortar.

The possible effect of emissions from cement-based mortar and cement-ash-based mortar slabs on perceived air quality was studied and compared by means of sensory assessments and chemical measurements. The tests were conducted on mortar samples alone and together with either carpet or linoleum. Air discharged from the CLIMPAQ-like glass chambers was assessed by twenty-five subjects and sampled on Tenax TA tubes for analysis by the GC/MS method. No significant differences were observed in odour intensity produced by cement-based mortar and cement-ash-based mortar slabs, and neither did they differ in chemical composition of the emissions. Odour intensity increased with the increased exposed area of mortar. A significant sink effect was observed when linoleum was added to any of the two slabs. The sink effect increased with the increased loading of the slabs. The combination of linoleum and mortar slabs resulted in lower odour intensity than that produced by any of the two materials when tested alone. A possible explanation is the uptake of organic acids emitted from linoleum by the mortar slabs, as the mortar is a strong base. A much weaker or no sink

effect was observed in the case when carpet was exposed together with the slabs. This was probably because carpet was not such a strong source of acids. The total concentration of organic compounds (TVOC) did not show any reasonable differences in concentrations of pollutants emitted by slabs alone or when they were together with linoleum and carpet. However, distinct differences were observed when the concentrations were considered based on the functional groups, e.g. organic acids, alkanes and alcohols.

Resumé

Overudnyttelsen af tilgængelige naturressourcer og dens mulige negative miljøpåvirkninger er fremherskende og omfattende problemer, som byggebranchen står overfor. Konkret er cement efter vægt den råvare, der bruges mest af i verden, næst efter vand, og under produktionen udledes 900 kg CO₂ pr. ton cement. Det voksende ønske om at reducere CO₂ emissionerne stimulerer cementindustrien til at finde materialer med lavt CO₂ fodaftryk, hvilket kræver erstatninger for cement. For at opnå mulige grader af cementsubstitution er det nødvendigt at anvende nye supplerende cementholdige materialer (SCM), som er lette at få fat i, og helst er lokalt tilgængeligt. Aske fra spildevandsslam (SSA) kan være en sådan bæredygtig ressource. En antagelse for undersøgelser, der gøres i nærværende arbejde er, at SSA, som et industrielt biprodukt, kan anvendes som en mulig erstatning for cement i cementbaserede materialer uden at kompromittere materialernes ydeevne. For at eftervise eller modbevise en sådan antagelse er der udført forskellige materialeundersøgelser, og forskellige metoder er bragt i anvendelse for at bestemme egenskaber for materialerne.

I Ph.D.-projektet er undersøgt delvis udskiftning af cement med SSA i mørtel og den virkning, det har på mørtlens hygrotermiske egenskaber samt indflydelsen på den indendørs luftkvalitet. Et overordnet formål med undersøgelsen har været at undersøge, hvordan mørtler med forskellige sammensætninger vekselvirker med indeklimaet. Derudover var målet at sammenligne metoder, der blev anvendt ved vurdering af hygroskopisk ydeevne af cementholdige materialer og deres indvirkning på den indendørs luftkvalitet. Dette har krævet en tværfaglig tilgang.

Projektets mål er opfyldt ved at udføre følgende tre hoved-forskningsopgaver: (1) Karakterisering af aske og undersøgelse af cementsubstitutionens virkning på udvalgte fysiske egenskaber ved mørtel. (2) Undersøgelse af effekten af askeindhold på mørtlens hygrotermiske egenskaber. (3) Sensoriske og kemiske målinger af emissioner fra mørtel samt mørtlens vekselvirkning af typiske forurenende stoffer i indeklimaet.

To SSA'er blev anvendt som erstatning for cement i undersøgelsen. De stammer fra to store danske forbrændingsanlæg beliggende i Avedøre og Lynetten i Storkøbenhavn-området. Virkningerne af forskellige forhold ved cementsubstitution i mørtel og to forbehandlingsmetoder for aske blev undersøgt.

Først og fremmest bekræftede resultaterne af karakterisering af SSA'er tidligere konklusioner om, at den kemiske sammensætning af SSA'er er meget variabel. Det blev også fundet, at SSA'ernes oprindelse fra nært beliggende spildevandsrensingsanlæg, ikke sikrer en sammenlignelig kvalitet. Desuden viste granulometrisk undersøgelse, at SSA'erne typisk bestod af større partikler sammenlignet med cementpartikler. Inkorporering af aske i cement-aske-baseret mørtel resulterede i mere porøse mørtelstrukturer sammenlignet med rent cementbaseret mørtel, hvilket påvirkede mørtlernes mekaniske

egenskaber, såsom trykstyrken. De hygroskopiske egenskaber af de individuelle bestanddele alene og af komplette mørtelprøver blev beskrevet ved sorptionsisotermer for vanddamp og ved en kapillær vandabsorptionsprøve. Selvom sorptionsevnen af de individuelle bestanddele var signifikant forskellig, havde askeindholdet kun en mindre virkning på sorptionsisotermerne for cement-aske-baseret mørtel. Vandabsorptionskoefficienten for mørtelprøver steg markant med forholdet mellem aske og cement. Dette indikerer, at den højere porøsitet af cement-aske-baseret mørtel har flere porer i det kapillaraktive område end rent cementbaserede mørtler.

De hygrotermiske egenskaber af cementbaseret og cement-aske-baseret mørtel blev undersøgt ved hjælp af forskellige tests, specifikt: varmeledningsevne, to hygroskopiske sorptionsforsøg og målinger af vanddamppermeabilitet. Målingerne viste, at den højere porøsitet af mørtel var årsag til en reduktion af varmeledningsevnen og en forøgelse af mørtlens vanddamppermeabilitet. Dette var forventet, da disse egenskaber afhænger af porøsiteten. Sorption blev testet ved to metoder: klimakammermetoden og desiccator-metoden. Observationerne viste, at sorptionsisotermerne var påvirket af den anvendte metode, dvs. indflydelse af CO₂ fra luften. Fremgangsmåden ved anvendelse af lukkede desiccator-beholdere af glas viste mindre eller ingen forskelle mellem cementbaseret og cement-aske-baseret mørtel, medens der blev observeret forskelle mellem mørtelblandingerne, når klimakammermetoden blev anvendt med sit atmosfæriske indhold af CO₂ i luften. Sammenligning af de to metoder viste, at den anvendte metode kan påvirke de målte parametre i en sådan grad, at de rapporterede resultater kan variere. Vurderingen af de hygroskopiske egenskaber af cementholdige materialer er ikke klart defineret i nogen standard og er ikke let at vurdere, idet den let kan påvirkes af forskellige faktorer. Der er et behov for at præcisere standardmetoder til hygrotermisk vurdering af cementholdige materialer.

Derudover blev der udført test af calciumcarbonat-indholdet (CaCO₃) for at detektere karbonatiseringens effekt på mørtelprøver. CaCO₃ blev påvist i alle mørtelprøver. Med hensyn til mørtelsammensætningen var CaCO₃-indholdet højest for rent cementbaseret mørtel.

Det sidste emne blev den mulige virkning af emissioner fra cementbaseret og fra cement-aske-baserede mørtelplader på den opfattede luftkvalitet undersøgt og sammenlignet ved hjælp af sensoriske vurderinger og kemiske målinger. Testene blev udført på mørtelprøver alene og sammen med enten tæppe eller linoleum. Luft, der blev udledt fra såkaldte CLIMPAQ - type glaskamre, blev vurderet af femogtyve forsøgspersoner og udtaget på Tenax TA rør samt analyseret ved GC/MS metoden. Der blev ikke observeret nogle signifikante forskelle i lugtintensitet afgivet af cementbaseret mørtel og cementaske-baseret mørtelplader, og der var heller ikke forskelle i emissionernes kemiske sammensætning. Lugtintensiteten steg med den emitterende mørteloverflades areal. Der blev observeret en betydelig evne til at optage lugt, når linoleum blev tilføjet i kombination med en af de to plader. Denne egenskab til at optage lugt steg med øget mængde mørtelplade. Kombinationen af linoleum og mørtelplader resulterede i lavere

lugtintensitet end den, der blev produceret af et af de to materialer, når de blev testet hver for sig. En mulig forklaring er mørtelpladernes optagelse af organiske syrer, der udsendes fra linoleum, da mørtlen er en stærk base. En meget svagere eller ingen evne til at optage lugt blev observeret i det tilfælde, hvor der blev opsat tæppe i kombination med mørtelpladerne. Dette var sandsynligvis fordi tæppet ikke var så stærk en kilde til afgivelse af syre. Den samlede koncentration af organiske forbindelser (TVOC) viste ingen væsentlige forskelle i koncentrationen af forurenende stoffer, der udsendes af pladerne alene, eller når de var sammen med linoleum eller tæppe. Der blev dog observeret tydelige forskelle, når koncentrationerne blev vurderet baseret på de funktionelle grupper, f.eks. organiske syrer, alkaner og alkoholer.

List of Abbreviations and Symbols

AM	Cement-ash-based mortar
AVE	Avedøre ash
A _w	Water absorption coefficients
Ca	Carpet
CM	Cement-based mortar (reference material)
G	Grinding pre-treatment method
IAQ	Indoor air quality
Li	Linoleum
LYN	Lynetten ash
PAQ	Perceived air quality
R	Raw/Untreated
REF	Cement-based mortar (reference material)
RH	Relative humidity
SCM	Supplementary cementitious material
SD	Standard deviation
SEM	Scanning electron microscope
SSA	Sewage sludge ash
VOC	Volatile organic compounds
W	Water washing pre-treatment method
XRF	X-ray fluorescence
δ	Water vapour permeability

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Chapter 1

Introduction

1.1 General Introduction

The field of sustainable buildings is rapidly developing and approaching towards becoming a more economical and ecological industry branch. In these areas, building development seeks to maintain high living standards and positive socio-economic trends while also seeking to minimize the irreversible destruction of nature. The focus has been shifted to increased energy efficiency of buildings and at the same time it has been appealed for preservation of natural resources. European and, in general, developed countries incline to use sustainable building materials and this tendency is growing. Besides that, a demand has been raised asking for utilization of waste and by-products encouraging their implementation into building constructions. The appropriate reuse of residues in different activity fields can make an important and beneficial contribution to reduction of environmental impact, e.g. by limiting the extraction of mineral resources and the associated energy consumption (extraction, transport, manufacturing, etc.) and by reduction of greenhouse gas emissions and waste. Redesigned construction materials may strongly support waste minimization in society, energy conservation and concurrently may contribute to sustainability of building constructions. One of the examples is concrete and its main constituent cement, used as a binder. Worldwide focus has been put on finding appropriate substitute for cement due to its specific environmental issues related to cement production, i.e. mining and CO₂ emissions. An alternative replacement may provide a feasible reduction of CO₂ footprint of concrete and its environmental load.

The so-called waste-based materials may offer huge potential benefits for the building industry in terms of costs or performance and at the same time contribute to the circular

economy, i.e. an economic system aiming at eliminating waste and the continual use of resources. However, they may be linked to a higher risk outside the main scope of building industry, e.g. an adverse effect on both outdoor and indoor environment. Potential risks related to this approach should not be overlooked. For example, application of polluting materials may lead to poor quality of indoor environment that may eventually cause a potential hazard for occupants' performance, well-being and health. Especially nowadays when lifestyle in developed countries is to spend most of the time indoors (Klepeis et al., 2001). Therefore, new building materials should undergo a comprehensive assessment process covering a wide range of material properties considering their effects on the environment and potential health risk. The aim of this work is to contribute with assessment and evaluation of material parameters and characteristics describing hygrothermal and sensory performance of mortars utilizing industrial by-product.

The present study was performed as a part of the ZeroWaste development area established at the Department of Civil Engineering, Technical University of Denmark. The ZeroWaste initiative intended to develop construction materials based on increased use of secondary resources such as products at the end of life cycle. This particular contribution dealt with use of incinerated SSA as cement substitute in mortar and its effect on mortar qualities. The overall motivation for the study was the fact that even partial replacement of cement may beneficially contribute to reduction of CO₂ footprint of mortar production and at the same time it may lessen a need of ash landfilling.

The following paragraphs outline the background and introduce in detail the motivation for the present dissertation work. Although mortar, not concrete, is a subject of the study, many references refer to concrete. Considering that mortar constituents are common with concrete, the background text often relates to concrete production.

1.2 Environmental Impact of Cement and Challenges of Secondary Resources

The cement industry belongs to the largest contributors to CO₂ emission caused by human activity. About 5–7% of global CO₂ emissions are from cement manufacturing plants. 900 kg of CO₂ are emitted to the atmosphere during production of one ton of cement (Benhelal et al., 2013). The CO₂ emission related to the concrete production, including cement production, is between 0.1 and 0.2 t per ton of produced concrete (Glavind and Munch-Petersen, 2000). With an annual global concrete production of approximately 3.8 billion cubic meters, concrete is the second most consumed substance in the world, after water (Sedgwick, 1991). Even if only a small percentage of the overall use of cement could be substituted by alternative hydraulic binders, it would have a huge positive effect on the environmental impact of concrete production. With the vast use of Portland cement, concrete production has a significant CO₂ footprint and currently represents 5% of the total global energy use in industry (Worrell et al., 2001).

The use of industrial by-products as alternatives to cement in concrete production reduces the need for landfilling and related costs, and consequently reduces the need to mine virgin raw materials. When secondary resources are used as partial cement replacements, the generic term used is “Supplementary Cementitious Material” (SCM) (Snellings et al., 2012). The main SCMs include coal fly ash, blast furnace slag, silica fume, volcanic ash and metakaolin. Since the 1990s, fly ash from coal combustion processes has widely been used as an SCM. However, many countries incline to other sources of energy rather than coal (Connolly, 2015; Lambert, 2016; Vaughan, 2016). In 2016 Great Britain claimed that the last coal power station in Britain will be forced to close in 2025 (Vaughan, 2016). Recently, six major countries, Canada, France, Germany, Austria, the Netherlands and Finland, announced the imminent phase-out of all coal-fired power-plants (Lambert, 2016). Canada has already reduced its coal use to about 7% and announced a phase-out of the resource by 2030 (Lou, 2016). France reduced the use of coal even to 3% and aims for phase-out of coal by 2023 (England, 2016). Smaller countries also plan to phase-out coal-fired power plants. Denmark, for instance, aims to phase out the use of coal for electricity generation by 2035 (The Danish Government, 2013). This implies that the interest in identifying other resources than coal fly ash was brought up also in the field of alternative cement substitutes.

An alternative to cement should be based on a high abundance of raw materials, low carbon emission, low energy consumption, low pollutant load and a possible use of waste products. Cleaner production, recycling and cement substitution are three effective approaches for the sustainable development of the concrete industry (Shen et al., 2017). One type of ash, which has shown potential as SCM is Sewage Sludge Ash (SSA) (Chen et al., 2006; Coutand et al., 2006; Donatello and Cheeseman, 2013; Halliday et al., 2012; Ing et al., 2016; Lynn et al., 2015; Monzó et al., 2003, 1996; Yusuf et al., 2012).

1.3 Sewage Sludge Ash and its Potential Use in Cement-Based Mortar

Sewage sludge refers to the residual, semi-solid material produced during sewage treatment of industrial or municipal wastewater. Approximately 10 Mt/year of dry mass sewage sludge is produced in European countries. However, incineration can reduce this amount by 70% by mass, and 90% by volume (“Eurostat - Tables, Graphs and Maps Interface (TGM) table,” 2015). The organic matter is combusted and by-products such as CO₂, other trace gases and water vapour are produced. The process of waste disposal by incineration is not complete since a non-negligible amount of residue of SSA remains afterwards.

Sewage sludge has been widely used in agriculture as a fertilizer because of its content of phosphorus. Recently, the tendency has been to incinerate it. It is estimated that the global production of SSA is approximately 1.7 million tons annually, mainly from the

USA, the EU and Japan, and it is expected to increase (Cyr et al., 2007; Murakami et al., 2009). A vast amount of SSA is currently being landfilled. Most SSAs are classified as waste, but it could also be regarded as a resource. Previous research has shown different options for the use of SSA in different construction materials: mortar, concrete, fired clay brick or lightweight foam materials (Ahmaruzzaman, 2010; Chen et al., 2013; Halliday et al., 2012; Kute and Deodhar, 2003; Lin et al., 2005; Lynn et al., 2015; Monzó et al., 2003, 1999, 1996; Smol et al., 2015; Wang et al., 2005; Wiebusch and Seyfried, 1997; Yusuf et al., 2012). Many of the applications simply use SSA as a direct substitute for raw materials such as clay or sand. However, the application of the greatest interest is the possibility of using SSA as a substitute of Portland cement, e.g. (Bazea-Brotons et al., 2014; Chin, 2016; Garcés et al., 2008; Ing et al., 2016; Lynn et al., 2015; Monzó et al., 2003, 1999, 1996; Yusuf et al., 2012), due to the considerable environmental benefits that would be achieved. Considering the cement annual production of 2.8 billion tons (Schneider et al., 2011), 0.6% of cement would be replaced if all SSA is used to substitute cement.

Summarizing previous findings, SSA has a porous microstructure and consists of irregularly shaped particles within silt and fine sand size fractions suggesting suitability as fine aggregate (Lynn et al., 2015). In ground form, the material's oxide composition and amorphous content indicates potential suitability for use as a cementitious material (Coutand et al., 2006; Cyr et al., 2007; Donatello et al., 2010a; Donatello and Cheeseman, 2013; Halliday et al., 2012; Lin et al., 2008; Ottosen et al., 2013a; Pan et al., 2003). Previous studies have demonstrated that Portland cement mortars made with SSA exhibit good mechanical properties (Monzó et al., 1999, 1996). An observed decrease in workability and strength (Chang et al., 2010; Garcés et al., 2008; Halliday et al., 2012; Monzó et al., 1999, 1996; Pan et al., 2003) can be offset by the addition of plasticizing agents (Monzó et al., 2003) or by adjusting the cement content to lower the water/cement ratio of the mix (Coutand et al., 2006; Halliday et al., 2012). However, at higher contents of SSA, the content of the phosphorus inhibits the setting time and the strength development (Nurse, 1952). In such a case, a treatment of an ash to extract phosphorus appears to be a reasonable option (Donatello, 2009; Ottosen et al., 2013b). Furthermore, the obtained phosphorus can also serve as a valuable resource for agricultural purposes.

1.4 Background Review for the Present Study

Generally saying, building materials have been investigated mostly for their mechanical and structural properties and some additional parameters of manufacturer's interest. However, other important properties pertaining to their impact on environment remain most often left behind. This dissertation work adds to the compiled knowledge on interaction of mortar with typical indoor climate. Specifically, reciprocal action with heat and humidity present in the air, alternatively with water, and on top of that, the effect

of the material on indoor air quality were investigated. The following paragraphs provide a short review of SSA use in mortar with focus on hygrothermal assessment and its effect on indoor air quality.

1.4.1 Ash Characteristics

Utilization of industrial residues such as ash brings many issues along. The chemical composition of SSA and its compound concentration are not consistent and depend on the composition of the initial source and the incineration process applied (Cyr et al., 2007). A majority of the publications report on oxide content as the crucial parameter of the ash. The main oxides in SSA are reported as SiO_2 , Al_2O_3 and CaO , whilst Fe_2O_3 , Na_2O , MgO , P_2O_5 , SO_3 and others are present in smaller quantities. A review by Lynn et al. (2015) shows that the majority of SSA samples fall around the latent hydraulic and pozzolanic regions, suggesting a potential for SSA use as a cementitious component in mortar/concrete. SSA is characterized by irregular particles and a porous microstructure, which may lead to high absorption and thus increase the water demand of concrete containing SSA (Monzó et al., 2003, 1996). One of the major concerns of using SSA is the content of heavy metals, which may cause deterioration to the cement-based material and represent an adverse environmental impact of the material. Of particular interest are significant contents of heavy metals such as As, Cd, Cr, Cu, Ni, Pb and Zn due to their toxicity (Lynn et al., 2018). Recently, research on ash utilization has focused on pre-treatment methods of the ash in order to stabilize potentially hazardous compounds, e.g. acid wash, water wash and heavy metals removal by electro-dialytic remediation (Kappel et al., 2018; Ottosen et al., 2013b). SSA may also contain high amounts of sulphur. Hence, a potential risk of concrete degradation due to sulphur attack should be taken into account when using sulphur-rich waste (Monzó et al., 1999).

There have been many studies of several different aspects of the use of SSA in concrete-related applications. A recent systematic review by Lynn et al. (2015) covered selected physical and chemical characteristics of SSA and its use in cement-based materials.

1.4.2 Hygrothermal Assessment of Mortar

Mortar is assumed to be able to transfer both heat and moisture by the mechanisms that occur in all porous materials. Several studies have been performed on moisture transfer in cementitious materials to describe the material behaviour under different experimental conditions and for different material compositions, e.g. (Abdelhamid et al., 2016; Carlier et al., 2012; Espinosa and Franke, 2006a, 2006b; Issaadi et al., 2015; Saeidpour and Wadsö, 2015a, 2015b, 2016; Anderberg and Wadsö, 2008; Pham, 2014a; Aimin, 1989; Baroghel-Bouny, 2007a, 2007b; Pham, 2014b). Some studies examined the influence of traditional mortar components by varying their proportions. Other studies dealt with variable composition of mortar or, in general, in cement-based materials. For example, Issaadi et al. (2015) reported on the water vapour sorption / desorption

isotherm for cement pastes, which had been cured for 7 days and 28 days, and for mortars with different water-cement and sand-cement ratios. As expected, they concluded that the sorption and desorption isotherms were dependent on the water-cement ratio (w/c) and that hysteresis could be observed over the whole range of relative humidity. Moreover, the storage capacity decreases with increasing age, as does the water vapour permeability. Only a few studies were found that dealt with mortar using SSA as cement substitute and at same time evaluated hygrothermal performance of the mortar (Alcocel et al., 2006; Baeza-Brotons et al., 2014; Fontes et al., 2004; Garcés et al., 2008). The results indicated that the partial replacement of Portland cement by SSA promoted an increase in the total porosity and a decrease of compressive strength at the age of 28 days of the reference cement-based mortar (Alcocel et al., 2006; Fontes et al., 2004; Garcés et al., 2008). However, with high content of SSA (30%), the mortar compaction became poor and higher water to binder ratio was suggested (Garcés et al., 2008). Water absorption coefficient was observed to be higher for mortar with SSA (Fontes et al., 2004). Baeza-Brotons et al. (2014) reported relation between density and capillarity stating that the density is closely linked to absorption. A decreasing tendency was observed in the density value while the water absorption coefficient increased with an increased amount of SSA, which may be due to the low density of the residue and the great amount of pores. The relation between both parameters was statistically demonstrated as significant.

A basic requirement for any hygrothermal assessment is knowledge of the dry mass of a sample. The dry mass is usually determined by exposing the sample to elevated temperature. However, the equilibrium moisture content of a cementitious material is strongly related to the temperature level, i.e. the apparent moisture content is dependent on the temperature at which the dry mass of the material is determined. Moisture is naturally present in the mortar structure at different energy levels, either in the form of water vapour in the pore air or as liquid water, which is either physically bound water (capillary water and adsorbed water) or chemically bound. When determining the amount of bound water, the evaporable water must be removed first (Nilsson, 1980). The content of evaporable water is commonly determined by drying at 105 °C under normal pressure conditions (Pham, 2014a, 2014b). However, this temperature may already modify the water content in hydration products and cause micro-cracks due to the tension of water in small pores (Nilsson, 1980). To avoid such damage, a good compromise to provide relatively quick drying is exposure to 40 °C as defined by standard (EN 13057, 2002). Pihlajavaara (1963) studied different effects on concrete weight changes: drying methods, temperature and relative humidity, and the effect of repeated cycles. His findings confirmed that especially small samples are more affected by carbonation than large samples because carbonation normally affects only a thin layer of material. In small samples, the carbonation process may be responsible for a weight gain in addition to that caused by sorption, and thus may misrepresent the actual weight.

Based on molar weight calculations, Pihlajavaara (1963) showed that there is an increase of carbonated cement paste in the range of a few % of the weight of the original paste, depending on the w/c ratio. He also compared two different drying methods: 1) specimens were stored in a climate chamber or 2) in a sealed desiccator. In both cases, the ambient air was almost the same. However, the air supplied to the climate chamber contained CO₂ while the air in the desiccator was still and sealed in a compartment. The results supported the previous statement of weight gain due to carbonation. Additionally, Pihlajavaara (1963) studied the effect of different storage conditions on the samples and how the sorption isotherms get affected by different w/c ratios of cement pastes. Pihlajavaara's results showed that the apparent equilibrium moisture content was higher in cement paste stored in the desiccators (at 25 °C) compared to cement paste stored in the climate chambers (at 21 °C).

As mentioned above, the carbonation process is another factor that affects the hygrothermal properties of cementitious materials. The carbonation process has two important consequences that arise from the chemical reactions involved: (i) a change of effective permeability due to microstructural changes and (ii) a reduction of the pH-value (Johannesson and Utgenannt, 2001). The permeability also changes with the content of alternative components, such as blast furnace slag or fly ash in blended cements, in which carbonation is also observed (Taylor, 1997). Pham (2014c) performed a study on the effects of carbonation on the microporosity and macroproperties of normalized mortar prepared with cement and compared two different techniques for determination of pore size distribution; nitrogen adsorption and water adsorption. The combination of both techniques showed that the volume of mesopores ($2 < r < 50$ nm) increased after carbonation due to the loss of micro pores ($r < 2$ nm). The changes in pores with radii larger than 50 nm were negligible. The practical implication of these microstructural changes is that it has consequences for the thermal properties, since changes in thermal conductivity were found to be related to both aspects: the water content in the samples, as dry samples have lower thermal conductivity than wet samples, and the carbonation/aging process. The increase in thermal conductivity during carbonation is due to the decrease in total porosity. Consequently, carbonated cement mortar has a higher thermal conductivity than non-carbonated mortar (Pham, 2014c).

In the hygrothermal testing of cementitious materials, another important effect is that repeated sorption/desorption cycles affect the mortar structure. This effect of sorption cycles was observed in a study by Pham (2014a) and takes place from the second cycle, as water molecules evaporated from the structure during drying at 105 °C return into the C-S-H microstructure during adsorption and cannot be desorbed afterwards even at a relative humidity under 10 %. This means that the desorption curve of the second cycle differs from that of the first cycle. When comparing the carbonated and non-carbonated samples, the sorption isotherms of carbonated samples are generally characterized by lower apparent moisture content than sorption isotherms of non-carbonated samples. The differential energy required to adsorb water molecules at material surfaces

is higher for carbonated cement mortar than for the non-carbonated one. The same conclusion was reported by Johannesson and Utgenannt (2001) who reported that the non-carbonated cement mortar holds more water at desorption than the carbonated sample.

1.4.3 Mortar, its Impact on Indoor Air Quality and its Air Cleaning Potential

Indoor air quality (IAQ), one of the environmental parameters, becomes one of major interests in buildings. It can impact the health, comfort, well-being, and productivity of building occupants (Bluyssen, 2009). It gets affected by many different factors, these include: sources of pollutants or odours; design, maintenance and operation of building ventilation systems; moisture and humidity (US EPA, n.d.). Over the past decades it has become evident that building materials are among major contributors to the pollution of the indoor environment with volatile organic compounds (VOCs), at least during the initial period after the construction or renovation of a building (Wolkoff, 1995). Building materials influence dynamic variation of pollutant concentrations in space by interacting with surrounding environment, known as the sink effect (adsorption and desorption phenomena on the surfaces) (An et al., n.d.), and by chemical transformation of pollutants on the surfaces and in the air.

For decades, the industry incorporated fly ash from coal combustion power stations as a supplementary cementing material (Chandra, 1997). However, very limited information was provided on the material pollution from mortar containing fly ash. A Danish study (Bødker, 2006a) compared the emissions from cement-based concrete and cement-ash-based concrete. Neither of the two studied concretes were sources of amines, alcohols and aldehydes. On the contrary, concrete cast to a form sprayed by mineral-based oil emitted hydrocarbons. The report also demonstrates sensory assessment of the studied concrete slabs and showed that they were associated with moderate to weak odour intensity that decreased over time.

It seems that coal fly ash was not worsening IAQ when used as cement substitute in mortar. Additionally, ash may possess some air cleaning properties similar to the activated carbon. Peloso et al. (1983) and Rovatti et al. (1988) investigated whether fly ash from coal combustion could be used as an adsorbent material for toluene vapour. The experiments showed that coal fly ash may indeed act as a possible adsorbent of toluene and, in general, organic gases and vapours, but only after suitable activation. These processes resulted in the coal ash acquiring adsorbing properties that were comparable with the usual but more expensive activated carbon. Whether adding fly ash that has undergone activation treatment to cement mortar can result in the product having air cleaning properties has not yet been investigated.

Only a few experiments have examined the interaction between cementitious materials and air pollutants. Most of them examined the possibility of air cleaning by adding photocatalytic additives, specifically TiO_2 , to existing materials (e.g. Calia et al., 2016;

Carp et al., 2004; Chen et al., 2011; Kolarik and Toftum, 2012; Nath et al., 2016; Sugrañez et al., 2013). Some studies focused on the interaction between cement-based mortar/concrete with various pollutants such NO_x, CO₂, and SO₂ (e.g. Bødker, 2006b; Decio et al., 2009; Iizuka et al., 2011; Martinez-Ramirez et al., 2002; Moghtaderi et al., 2012; Ramakrishnan and Orlov, 2014). Decio et al. (2009) examined the interaction of three mortar mixtures with VOCs. The results revealed that all three mortar types reduced the total concentration of VOCs (TVOC) during a 24-h test. In addition, the mortar containing natural pozzolana (i.e. siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (ASTM 618-08, 2008), e.g. volcanic ash) caused the largest reduction in TVOC compared to the other two mortars. This effect could be due to the different composition of the mortar and the use of a natural material that results in higher porosity: The pictures from the scanning electron microscope revealed that a greater superficial area was available for adsorption. Decio et al. (2009) postulated that various reductions of TVOC in the presence of mortars can be caused not only by differences in porosity and in physical characteristic of the mortars, but also by chemical reactions. This postulation was based on results that showed that the VOCs detected in the presence of mortar containing natural pozzolana differed from those detected in the presence of other mortars. However, no more details of the examinations and procedures were provided.

Other studies investigated interaction of mortar with outdoor pollutants, specifically NO_x, an ambient pollutant associated with the traffic. Even though, the presence of outdoor pollutants is outside the scope of the present work, it is worth mentioning few case studies to outline air cleaning potential of mortar. The Green Concrete project examined the interaction of concrete with NO₂ produced by traffic (Bødker, 2006b). Concrete with and without TiO₂ additive was investigated and the tests indicated that there was a limited effect of photocatalytic reaction on NO₂ removal. The results also revealed that the concrete without TiO₂ additive and even under complete darkness can reduce NO₂ concentration. Another study on NO₂ adsorption of newly casted and aged concrete was carried out by Ramakrishnan and Orlov (2014). They found out that concrete made of Portland cement, limestone, sand, gravel, fly ash and water, has the adsorption capacity resulting in measurable NO₂ reduction. The decrement of the uptake with the increase of the concrete age was observed. The relative humidity (RH) also affected the NO₂ uptake: Significantly smaller uptake of NO₂ was observed in the dry conditions (0 % RH) - the uptake was then only 5% to 10% of the NO₂ uptake at 50% RH. Ramakrishnan and Orlov (2014) explained this phenomenon by neutralization of high pH alkaline concrete surface as a result of nitrate (NO₃⁻) and nitrite (NO₂⁻) formation inducing changes of material composition on the surface. Neutralization of alkaline pH of newly casted concrete can also be caused by naturally occurring carbonation process (Johannesson and Utgenannt, 2001). Newly cast concrete has significant

concentration of calcium hydroxide ($\text{Ca}(\text{OH})_2$) on the surface (called slake lime or caustic lime) which converts to calcium carbonate (CaCO_3) and thus reduces pH of the pore water in hardened mortar with the increasing age because of naturally occurring reaction with the adjacent CO_2 . This may indicate that air cleaning ability of cementitious materials is dependent on the age of material.

1.4.4 Summary and Research Needs

- The chemical compositions of SSAs and their compound concentrations are not consistent, therefore, it is of great benefit to accompany research publication on utilization of SSA by XRF analysis of ash. It may help to understand material behaviour in the latter research steps and material testing.
- Only few studies reported on hygrothermal assessment of mortar where cement was partially substituted by SSA, mostly they focused only on one or two relevant parameters. A consistent study summarizing hygroscopic behaviour of mortar containing SSA is clearly missing. The effect of SSAs originating from different wastewater treatment plants and various substitution ratios on hygrothermal characteristics of mortar needs to be further investigated.
- Several conditions have significant effect on weight and structural changes of cementitious materials, e.g. drying method, exposure to different relative humidity, carbonation, etc. Standard procedures and conditions of hygrothermal assessment of cementitious materials are not clearly defined in any standard. Thus, experimental outcomes from different studies are not comparable and unequivocal because experiments are not performed under uniform conditions. The investigation of experimental conditions and an impact of applied methods on results of hygrothermal behaviour of mortar containing SSA would be a contribution to prospective testing guidelines.
- Interaction between cementitious materials and indoor climate has not been sufficiently studied. Only limited information was provided on the material pollution from mortar in general and its effect on odour intensity. It has been shown that concrete w/ and w/o coal fly ash was not source of amines, alcohols and aldehydes. Additionally, it was associated with moderate to weak odour strength. However, there was no work identified that would deal with impact of mortar containing SSA on human perception and material emissions. This represents a gap in compiled knowledge of material characteristics with respect to material interaction with indoor environment and its impact on perceived air quality (PAQ).
- Cementitious materials have been investigated as potential adsorbents of pollutants by very few researchers. Some air cleaning potential has been reported when material was in contact with typical outdoor pollutants such as NO_x , SO_2

and CO₂. Another experiment showed capability of coal fly ash to act as a possible adsorbent of toluene and, in general, organic gases and vapours. The only study was found to report reduction of TVOC concentration in presence of mortars, however, this phenomenon was not investigated any further. Reduction of pollutant concentrations, specifically VOC concentrations, is among the main goals of indoor climate research as it may significantly contribute to an improvement of IAQ and may result in reduction of costs related to ventilation rates.

1.5 Hypothesis and Objectives

A general assumption of the present work has been that partial substitution of cement by sewage sludge ashes (SSAs) in mortar will contribute to reduction of CO₂ emissions from cement production and will minimize the need for landfilling of ash. Provided that partial substitution of cement with SSA will have no or only minimal negative effects on the quality, structure and properties of mortar.

The main objective of the study was to investigate the consequences of partial cement substitution by SSA on parameters of mortar with respect to its interaction with indoor environment. An interdisciplinary approach was applied in order to cover broad scope of the project. It has been a deliberate choice to adopt knowledge from various sciences, i.e. material science (behaviour of cementitious materials, composition), material structure (porosity, strength), building physics (heat and mass transfer), indoor environment quality and human perception (material odours, sensory perception, emissions) and chemistry of material emissions (identification of VOCs). The interconnection of these subjects should bring a distinct insight into material testing and its outcomes. Rather than going very much into details with each specific field, the study has aimed at showing relations between the different sciences and their mutual importance.

Three overarching research questions were setup as follows with associated activities:

How does SSA grain characteristics differ from those of cement grains? How does cement substitution by SSA affect mortar structure?

- In order to see differences in particles of cement and ash, specific grain characteristics should be determined; i.e. chemical composition, grain size distributions, sorption ability of ash and cement.
- Physical parameters of cement-ash-based mortar, i.e. density, porosity, capillary sorption and compressive strength, should be compared to those of cement-based mortar to be able to assess the effect of ash content on mortar structure.

How does cement substitution by SSA affect hygrothermal characteristics of mortar? Are the currently used hygrothermal test methods applicable for assessing alternative cementitious materials?

- The affinity of cement and ash to water vapour and its effect on sorption ability of mortar should be examined to see how ash content affects hygroscopicity of mortar samples.
- In order to assess the suitability of the test methods for determination of hygroscopic properties, various methods and set-ups should be performed and compared.
- The ability of the mortar to absorb and release heat and water vapour should be determined to be able to compare heat and moisture transfer in cement-based vs. cement-ash-based mortar.
- In order to understand the modification of mortars of different composition that occurs when exposed to natural humid environment, suitable tests should be performed to clarify the influence of carbonation.

How does cement substitution by SSA affect chemical emissions and odours released from mortar? How do methods of sensory and chemical assessment compare?

- Sensory and chemical assessment should be carried out to study emissions released from mortar samples and their effect on indoor air quality.
- The interaction between mortar samples and typical indoor pollution sources should be investigated in order to study air cleaning potential of mortars with various compositions.
- Reciprocal correlation between sensory and chemical assessments of material emissions should be evaluated by comparison of the outcomes achieved from both methods.
- Values of TVOC, functional groups of VOCs and outcome from sensory measurements should be compared to recognize a reliable indicator of potential negative effects of building materials on indoor air quality.

1.6 Organization of the Thesis

An overview of the chapters and the list of publications (JP – journal paper, CP – conference paper, EA – extended abstract) and the eventual collaborations are briefly presented in Table 1.1. The thesis is solely based on the journal papers present in the Appendix and has been put in the format where summary of methods, results, discussions and conclusions is merged in the relevant chapters of the thesis.

Table 1.1 *An overview of the chapters and the relevant papers in collaboration with other researchers throughout the Ph.D. project.*

Chapter	Reference	Title	In collaboration with
I	Thesis	Introduction	---
II	Thesis	Methods	---
III	Thesis	Results	---
IV	Thesis	Discussion and Implications	---
V	Thesis	Conclusions	---
Appendix	JP1	Characterization of sewage sludge ash and its effect on moisture physics of mortar (Journal of Building Engineering, 2019)	<u>Lisbeth M. Ottosen</u> , <u>Gunvor M. Kirkelund</u> , <u>Carsten Rode</u> , <i>Technical University of Denmark (DTU), Denmark</i> , <u>Ruut H. Peuhkuri</u> , <i>Aalborg University, Denmark</i>
	JP2	Determination of hygrothermal parameters of cementitious mortar: The effect of partial replacement of cement by incinerated sewage sludge ash (Journal of Building Physics, 2018)	<u>Ruut H. Peuhkuri</u> , <i>Aalborg University, Denmark</i> <u>Carsten Rode</u> , <i>Technical University of Denmark (DTU), Denmark</i>
Appendix	JP3	The Effects of Cement-Based and Cement-Ash-Based Mortar Slabs on Indoor Air Quality (Building & Environment journal, 2018)	<u>Pawel Wargocki</u> , <u>Jakub Kolarik</u> , <i>Technical University of Denmark (DTU)</i>

The list of additional publications that were issued in the period of the Ph.D. study. Due to the broader scope of the conference papers and their remote link to the thesis' topic, the following publications were not included in the thesis. They can be found in the corresponding proceedings.

	CP1	Incinerated sewage sludge ash as alternative binder in cement-based materials; effect on mortar characteristics (proceedings of WASTES: Solutions, Treatments and Opportunities conference, 2013)	<u>Lisbeth M. Ottosen</u> , <u>Per Goltermann</u> , <u>Kamil Hodicky</u> , <i>Technical University of Denmark (DTU)</i>
	CP2	Waste-based materials; capability, application and impact on indoor environment – Literature review (proceedings of Indoor Air 2014 conference)	<u>Carsten Rode</u> , <u>Jakub Kolarik</u> , <u>Pawel Wargocki</u> , <i>Technical University of Denmark (DTU)</i> <u>Ruut H. Peuhkuri</u> , <i>Aalborg University, Denmark</i>
	CP3	Determination of diffusion parameters using a semi-dynamic dual chamber method (proceedings of Healthy Buildings 2015 America conference)	<u>Guoqing He</u> , <i>Zhejiang University, China</i> , <u>Carsten Rode</u> , <i>Technical University of Denmark (DTU), Denmark</i> , <u>Jianshun Zhang</u> , <i>Syracuse University, USA</i>

EA	Sensory ratings of emissions from non-traditional building materials (proceedings of Indoor Air 2016 conference)	<u>Jakub Kolarik</u> , <u>Carsten Rode</u> , <u>Pawel Wargocki</u> , <i>Technical University of Denmark (DTU)</i> <u>Ruut Peuhkuri</u> , <i>Aalborg University, Denmark</i>
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Chapter 2

Materials and Methods

To meet the objectives of the Ph.D. study the following actions were taken: (1) Pre-treatment of two studied ashes and preparation of mortar samples (JP1, JP2, JP3), (2) Ash characterization and investigation of its effect on structure of mortar (JP1), (3) Hydrothermal assessment of mortar (JP1, JP2) and (4) Investigation of the effect of mortar on indoor air quality and its air cleaning potential (JP3). This chapter presents mortar recipes and provides brief description of testing methods and experimental procedures. More details can be found in the relevant papers attached in the Appendix.

2.1 Studied SSAs, their Pre-treatment and Preparation of Mortar Samples

2.1.1 Origin of the Incinerated Sewage Sludge Ashes

SSAs from the two major Danish incineration plants were used in the project. The sludge incinerated at both plants originated from municipal wastewater treatment processes. Iron was used in both facilities to precipitate phosphorus, and the sewage sludge was incinerated in a fluidized bed combustor at about 850 °C. Specifically, the SSAs were from Avedøre Wastewater treatment plant (AVE) and from Lynettefællesskabet (LYN) (Figure 2.1 a) and b) respectively). Both plants are located in Denmark, close to the capital Copenhagen. The plants treat wastewater from 17 municipalities that cover approximately 1,375,000 inhabitants. After sampling, the ashes were stored in closed plastic containers at room temperature.

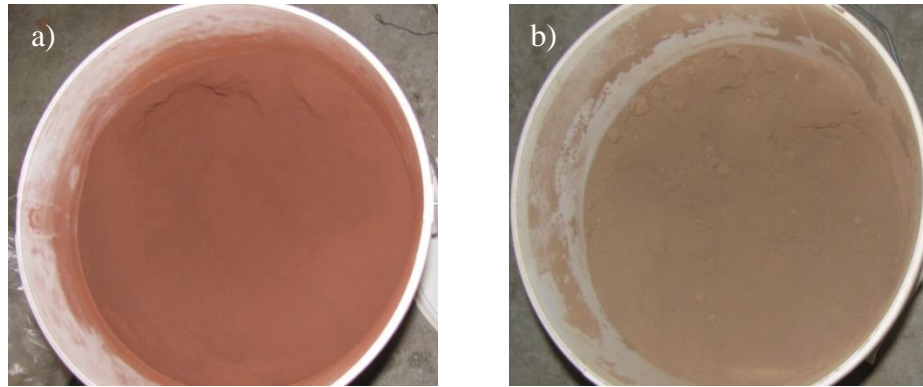


Figure 2.1 The two investigated SSAs: a) Avedøre ash (AVE) and b) Lynetten ash (LYN).

2.1.2 Pre-treatment Methods of SSAs

Two pre-treatment methods for SSA were applied in this study; water washing (W) or grinding (G). Water washing of SSA consisted of 3 washing cycles in distilled water. 100 g of ash was mixed in a 1L plastic bottle with 500 ml of distilled water and agitated for 1 min. Afterwards the bottle was placed in a vertical position until the SSA settled. When settled, water was decanted and the bottle was refilled with a new dose of 500 ml distilled water. This procedure was repeated 3 times. During the last turn, water together with SSA was decanted through a filter paper (11 μm) (Figure 2.2 b)) and the wet SSA was dried in an oven at 105 °C for period of 48 hours when constant mass was reached. In the latter pre-treatment method, SSA was grinded for 30 sec in a Vibrating Cup Mill Pulverisette 9 (Figure 2.2 a)). After grinding, the ash was dried in an oven at 105 °C.



Figure 2.2 a) Ash grinding; ash placed in a cup with grinding rings b) Water washing of ash

2.1.3 Preparation of Mortar Samples

Reference mortar samples based on cement were prepared according to the standard DS/EN 196-1 (2005). For the mortars containing SSA, the same basic recipe was used,

but part of the cement content was replaced by SSA (see Table 2.1 for recipes and Table 2.2 for resulting samples). Basic Aalborg Portland cement was used as a binder (Portland limestone cement, strength class 52.5 N). The sand by Dansand A/S was used in the recipe and met the requirements defined by the standard with median diameter $D(0.5) = 0.516$ mm.

Table 2.1 *Basic mortar recipes used in this work.*

Substitution ratio [%]	Cement [g]	SSA [g]	Sand [g]	Water [g]
0 (Ref)	450	0	1350	225
10	405	45	1350	225
30	315	135	1350	225

Table 2.2 *A matrix of mortar mixtures used in the study. Names of the samples come from ash origin (AVE or LYN), substitution ratio (10 or 30) and pre-treatment method (G or W).*

Name	Substitution ration [%]	Ash origin	Pre-treatment
REF	0	X	X
AVE 10G	10	Avedøre (AVE)	Grinding (G)
AVE 10W	10	Avedøre (AVE)	Water-wash (W)
LYN 10G	10	Lynetten (LYN)	Grinding (G)
LYN 10W	10	Lynetten (LYN)	Water-wash (W)
AVE 30G	30	Avedøre (AVE)	Grinding (G)
AVE 30W	30	Avedøre (AVE)	Water-wash (W)
LYN 30G	30	Lynetten (LYN)	Grinding (G)
LYN 30W	30	Lynetten (LYN)	Water-wash (W)

2.2 Ash Characterization and its Effect on Mortar Quality

2.2.1 Ash Characterization

The characterization and extraction experiments were always performed using ash that had been dried at 105 °C for at least 24 h. An external, commercial laboratory performed XRF analysis. The morphology was studied by means of a Scanning Electron Microscope (SEM) on either ground or water washed ash. Particle size distributions were measured by laser diffraction using Malvern Mastersizer 2000. A dry dispersion method for moisture sensitive materials was used.

2.2.2 Water Vapour Adsorption Test of Cement and SSAs

A determination of the hygroscopic sorption properties of cement and ashes was performed in accordance with the standard ISO 12571 (2000). The standard specifies two alternative methods, using either a desiccator or a climatic chamber. In this case a method using glass desiccators was used for determination of the absorption isotherm. The relative humidity in each desiccator was maintained with different salt solutions with the following steps: 33%, 58%, 75%, 86% and 94%.

2.2.3 Apparent Density and Open Porosity of Mortar Samples

Measurements of apparent volume V_o and open porosity P_o followed standard DS/EN 772-4 (1998). The apparent density ρ_o considers the solid constituents of the material and the pores in combination. It is defined as the ratio of the dry mass M_{dry} and the volume V_o of the dry specimen. The open porosity or void ratio is the percentage of open pores in the specimen. The test was run using prisms of 4×4×8 cm.

2.2.4 Compressive Strength Test of Mortar Samples

The compressive strength was measured according to the procedure described in the standard DS/EN 196-1 (2005). The work involved testing of samples based on nine different mixtures, see Table 2.2. The substitution ratio of cement varied from 0% (REF) to 10% and 30%. The compressive strength of the mortar samples was assessed after 28 days of curing for six replicates of 4×4×8 cm monolithic prisms.

2.3 Hygrothermal Assessment of Mortar

2.3.1 Thermal Conductivity and Volumetric Heat Capacity

The thermal conductivity and volumetric heat capacity were determined under laboratory conditions at an average temperature of 24 °C using a heat transfer analyser, ISOMET 2104. Measurements were performed with a surface probe with a disc sensor on samples with dimensions 30×30×3 cm.

2.3.2 Sorption and Moisture Fixation

The hygroscopic sorption properties of mortar samples were measured in accordance with the standard ISO 12571 (2000). The standard specifies two alternative methods that can be used, that is: the desiccator method and the climatic chamber method. Both methods were applied. Moisture storage in the hygroscopic range was determined by exposing the samples to various levels of relative humidity (RH) until equilibrium level had been reached. RH levels set in the climatic chamber were the following: 11%, 30%, 50%, 70%, 85%, 93% and 96%, and in the desiccators it was as follows: 33%, 58%,

75%, 86% and 94%. The mortar samples were crushed into grains with a maximum size of 5 mm and dried at 45 °C.

2.3.3 Water Vapour Permeability

The water vapour permeability was determined experimentally using the cup method. RH gradient was created in such a way that a steady one-dimensional transport across the samples was attained, as described in the standard ISO 12572 (2001). In dry cup tests, silica gel was used as a desiccant to achieve low RH close to 0%, while potassium nitrate (KNO_3) was used to generate a high RH of $93\% \pm 0.66\%$ in the wet cups. All the assemblies were placed in a temperature- and humidity-controlled chamber and exposed to constant conditions of temperature 23 ± 1 °C and RH $53\% \pm 3\%$. By regular weighing, the rate of water vapour transmission was determined.

2.3.4 Capillary Water Absorption

The water absorption test followed standard ISO 15148 (2002). The samples were partially immersed in water so that only the bottom side was in contact with the water. The weight gain of the samples due to water absorption was determined over time at increasing intervals. The water absorption coefficient A_w is expressed as a mass of water absorbed by a test specimen per surface area and square root of time.

2.3.5 Carbonation Test

Dry mortar samples were ground into 'flour-like' powder and immersed in a hydrochloric acid (HCl) solution. Calcium carbonate CaCO_3 , a product of carbonation, reacted with hydrochloric acid to form calcium chloride (CaCl_2), carbon dioxide (CO_2) and water. The concentration of CO_2 was measured and based on that the content of CaCO_3 was calculated.

2.4 Mortar, its Impact on Indoor Air Quality and its Air Cleaning Potential

2.4.1 Materials

Emissions from cement-based and cement-ash-based mortar samples were tested singly and together with either carpet or linoleum. Specifically, a standard cement-based mortar made of a cement-sand mixture (abbreviated as CM) and a cement-ash-based mortar (abbreviated as AM) where 30% of the cement content had been replaced by SSA from Avedøre Wastewater treatment plant. On the contrary to hygrothermal assessment, in this case, only mortar with substitution of 30% of cement was tested based on the assumption of maximum potential effect of SSA content on odour strength and material emissions. The mortar recipe was described in the previous paragraph 2.1.3. Linoleum

(abbreviated as Li) and carpet (abbreviated as Ca) were chosen as two typical materials representing indoor wall-to-wall floor coverings.

2.4.2 Experimental Facilities and Experimental Conditions

The experiments were carried out in the twin stainless steel climate chambers at DTU (Albrechtsen, 1988). Each chamber had a floor area of 9 m², a height of 2.5 m and a volume of 22.5 m³. They were ventilated using underfloor air distribution that supplied 100% outdoor air, with exhaust outlets in the ceiling. The samples of the materials tested in the present experiments were placed inside seven ventilated 200 L glass chambers (40×50×100 cm) located in the stainless steel chambers. These, CLIMPAQ-like glass chambers had been used for many other experiments studying material emissions and were described by Gunnarsen et al. (1994). The chambers were made of glass on metal support racks. Two ventilators were attached on the top of each glass cover to ensure that the chambers were well ventilated. The air was extracted via a diffuser allowing for sensory and chemical measurements of the air exhausted from the chamber.

The steel chambers were ventilated with a maximum outdoor airflow resulting in the outdoor air change rate of 50 h⁻¹. The air temperature was set to 23 °C. Relative humidity was not controlled and varied during experiments between 13% and 32%. The glass chambers were ventilated with the air supplied to the steel chambers. The inlet airflow was set to be about 0.9 L/s and the air velocity at the top of diffuser in the glass chamber where the sensory and chemical measurements were performed was about 0.2 m/s. All the glass chambers were covered with aluminium foil during the experiments so that their content was invisible for the subjects performing the sensory assessments. The loading of materials in the glass chambers were designed in accordance with the Nordtest method described in NT Build 482 Report (Nordtest, 1998). The specific loadings and material setup are present in Table 2.3. In total, 18 conditions were tested in the present experiment.

Table 2.3 *Experimental plan including material setup and loadings; CM=cement-based mortar; AM-cement-ash-based-mortar; Li=linoleum; Ca=carpet.*

Experimental matrix								
Mortar loading [m ²]	CM	CM + Li	CM + Ca	AM	AM + Li	AM + Ca	Li	Ca
1.4	•	•	•	•	•	•	•	•
1.9	•	•		•	•			
2.8	•	•	•	•	•	•		

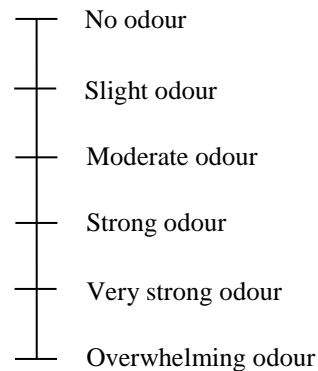
In one of the glass chambers, 2-propanone was evaporated passively so that its concentration was constant at about 80 ppm; the concentration was measured using an Innova 1312 gas monitor. 2-propanone exposure was used as a reference condition to examine whether any changes in the performance of the sensory panel performing sensory assessments occurred during the course of experiment.

2.4.3 Sensory Measurements

Each experimental condition was assessed by a sensory panel, see Figure 2.4 a). The sensory panel consisted of twenty-five subjects (13 males and 12 females). They were 22 – 38 years old, all university students, non-smokers, and not suffering from asthma, allergies, or other chronic diseases.

The subjects assessed odour intensity, the acceptability of the air quality, air freshness, pleasantness and nose irritation. Only the ratings of odour intensity were analysed in detail and published. The odour intensity scale (Yaglou et al., 1936) shown in Figure 2.3 was used to obtain sensory measurements of odour intensity.

Figure 2.3 *Odour intensity scale. The scale was coded as follows: 0 – No odour, 1 – Slight odour, 2 – Moderate odour, 3 – Strong odour, 4 – Very strong odour, 5 – Overwhelming odour.*



2.4.4 Chemical Measurements

The air used in the chemical analysis was withdrawn from the glass chambers through Tenax TA sorbent tubes inserted into a diffuser, see Figure 2.4 b). Double sampling was made; the volumes sampled were 3 L and 4 L. The airflow rates through the tubes were 0.1 L/min and 0.08 L/min respectively; they were controlled by calibrated pumps. A 3 L sampling was additionally made of the background air in the chamber. Blanks were made and analysed, too. The samples were analysed using TDS-GC-MS method according to ISO 16000-6 (2011) by an external certified laboratory. The concentrations were calculated as toluene equivalents with a lower reporting limit of 1 $\mu\text{g}/\text{m}^3$.

In the conditions in which cement-ash-based mortar samples were present there could have been ammonia emissions due to the ash processing. Two conditions with such samples at the highest mortar loading of 2.8 m^2 were therefore examined for ammonia

according to the guidelines relevant for organic recycled materials and ash-made concrete as defined by the National Institute for Occupational Safety and Health (NIOSH) (“CDC - NIOSH Pocket Guide to Chemical Hazards - Ammonia,” n.d.). The method is based on a solid sorbent tube, sulfuric acid-treated silica gel, and spectrophotometry.



Figure 2.4 a) Subject sniffing and a glass chamber covered with aluminium foil. b) Sampling by Tenax TA tube.

2.4.5 Procedures

The sensory evaluations of the air extracted from the chambers with samples of mortar, flooring materials and their combinations were carried out on eight non-consecutive days in March and April 2015. The glass chambers in the climatic chambers were loaded with the tested materials on the day prior to each experimental session and sealed with an aluminium low-emitting tape. Subjects were asked one-by-one to perform an evaluation. After entering the chamber, they approached the diffuser and inhaled the air exhausted from the chamber through it. Only one inhalation was made, after which they rated odour intensity, the acceptability of the air quality, irritation, freshness and pleasantness of the air. Then they left the chamber and took a 1–3 minute break in the ventilated space before the next evaluation. The subjects performed 9 evaluations on one day and a total of 72 evaluations during the eight-day experiments. Besides assessments of the air extracted from the chambers they also assessed the air in each climatic chamber. The order in which the evaluations were made was randomized for all subjects.

Chemical sampling was performed on the same samples and with an identical glass chamber setup one year after the sensory experiment. Identical procedures were applied for conditioning the samples as in the case of the sensory assessments.

2.4.6 Statistical Analyses

Statistical software R version 3.3.1 (R Core Team, 2015) was used to analyse the results of the sensory assessments. A Linear Mixed Effects (LME) model (Laird, 1982) was used to analyse the influence of the different types of mortar, the amount of mortar

present (loading) and the presence/absence of linoleum/carpet on the odour intensity assessed by the subjects. In addition, pair-wise comparisons were made using the Wilcoxon matched-pairs signed-ranks test to compare linoleum and carpet alone and in combination with mortar, and to investigate differences between mortars at a specific loading. The level for rejection of the Null Hypothesis was set at $P = 0.05$ (2 tail).

2.5 Summary of Experimental Methods

Table 2.4 *Table of applied methods, apparatuses and standards.*

Objective	Method/Apparatus	Standard	Performed
Chemical characterization of ash	X-ray fluorescence (XRF)	X	Commercial laboratory
Morphology	Scanning Electron Microscope (SEM)	X	DTU lab
Particle size distribution	Dry dispersion/Malvern Mastersizer 2000	X	DTU lab
Apparent density, open porosity		DS/EN 772-4	DTU lab
Compressive strength		DS/EN 196-1	DTU lab
Capillary water absorption		ISO 15148:2002	DTU lab
Drying	Oven, Desiccator, Climatic chamber	X	DTU lab
Thermal conductivity	ISOMET 2104	X	DTU lab
Sorption isotherms	Desiccator, Climatic chamber	ISO 1257:2000	DTU lab
Water vapour permeability	Cup method	ISO 12572:2001	DTU lab
Carbonation	Immersion in hydrochloric acid	X	DTU lab
Sensory assessment of emissions	Human Subjects, Glass chambers	NT Build 482	DTU lab
Chemical assessment of emissions	Tenax TA, TDS-GC-MS	ISO 16000-6	Commercial laboratory

Chapter 3

Results

Results presented in this chapter represent highlights of the experiments, more details can be found in the journal papers in the appendix. This chapter is divided into three subchapters; 3.1 Ash characterization and its effect on mortar quality (JP1), 3.2 Hygro-thermal assessment of mortar (JP1, JP2) and 3.3 Impact on indoor air quality and its air cleaning potential (JP3).

3.1 Ash Characterization and its Effect on Mortar Quality

3.1.1 Chemical Characteristics of the SSAs

The bulk element oxide concentrations are shown in Table 3.1. Both ashes contained SiO_2 , CaO and Al_2O_3 , which are also major compounds of ordinary cement. However, the pozzolanic activity of the two ashes was not explicitly studied but it is assumed that the pozzolanicity of SSAs is low compared to that of cement. In general, the oxide contents of the two studied ashes varied within a typical range of concentration values or were just in the low end of the range.

Table 3.1 *Major oxide content and chloride content present in the cement, coal fly ash and SSAs.*

Major oxide content [%]	Cement	Coal fly ash*	Avedøre not treated	Lynetten not treated	SSA**
MgO	0.53	0.1-6.7	1.82	1.99	0.02-23.4
Al ₂ O ₃	4.91	2.6-20.5	4.4	2.65	4.4-34.2
SiO ₂	20.1	11.8-46.4	15.83	14.33	14.4-65.0
CaO	65.8	15.1-54.8	23.37	36.38	1.1-40.1
TiO ₂	0.35	0.6-1.0	0.83	0.67	0.3-1.9
Fe ₂ O ₃	5.43	1.4-15.6	16.30	7.15	2.1-30.0
MnO	0.04	0.1-6.7	0.09	0.05	0.03-0.9
K ₂ O	0.81	0.3-9.3	1.45	1.81	0.1-3.1
Na ₂ O	<0.67	0.2-2.8	0.67	0.81	0.01-6.8
P ₂ O ₅	0.23	0.2-0.4	18.33	10.31	0.3-26.7
SO ₃ ⁻	4.74	1.4-12.9	2.00	4.74	0.01-12.4
Cl ⁻	0.1	--	<0.01	0.2	--

*Source: Hemalatha and Ramaswamy (2017) (coal fly ash Class C, mainly siliceous fly ash)

** Source: Cyr et al. (2007) (range of typical min and max values based on literature review)

3.1.2 Particle Size Distribution of Cement and SSA

The grain size distribution for cement, SSAs and sand are seen in Figure 3.1. Cement has finest grains, while LYN is clearly characterized by finer particles compared to AVE, both in the as-received form (R) and when it had been ground (G). Figure 3.1 a) shows that after 30 sec of grinding, the particle size distribution curve was shifted and became closer to that of cement, compared to non-ground samples. In Figure 3.1 b), the water-washed (W) ashes follow the curve of untreated ash which suggests that water-washed particles were not flushed out and even the smallest particles were captured on the filters.

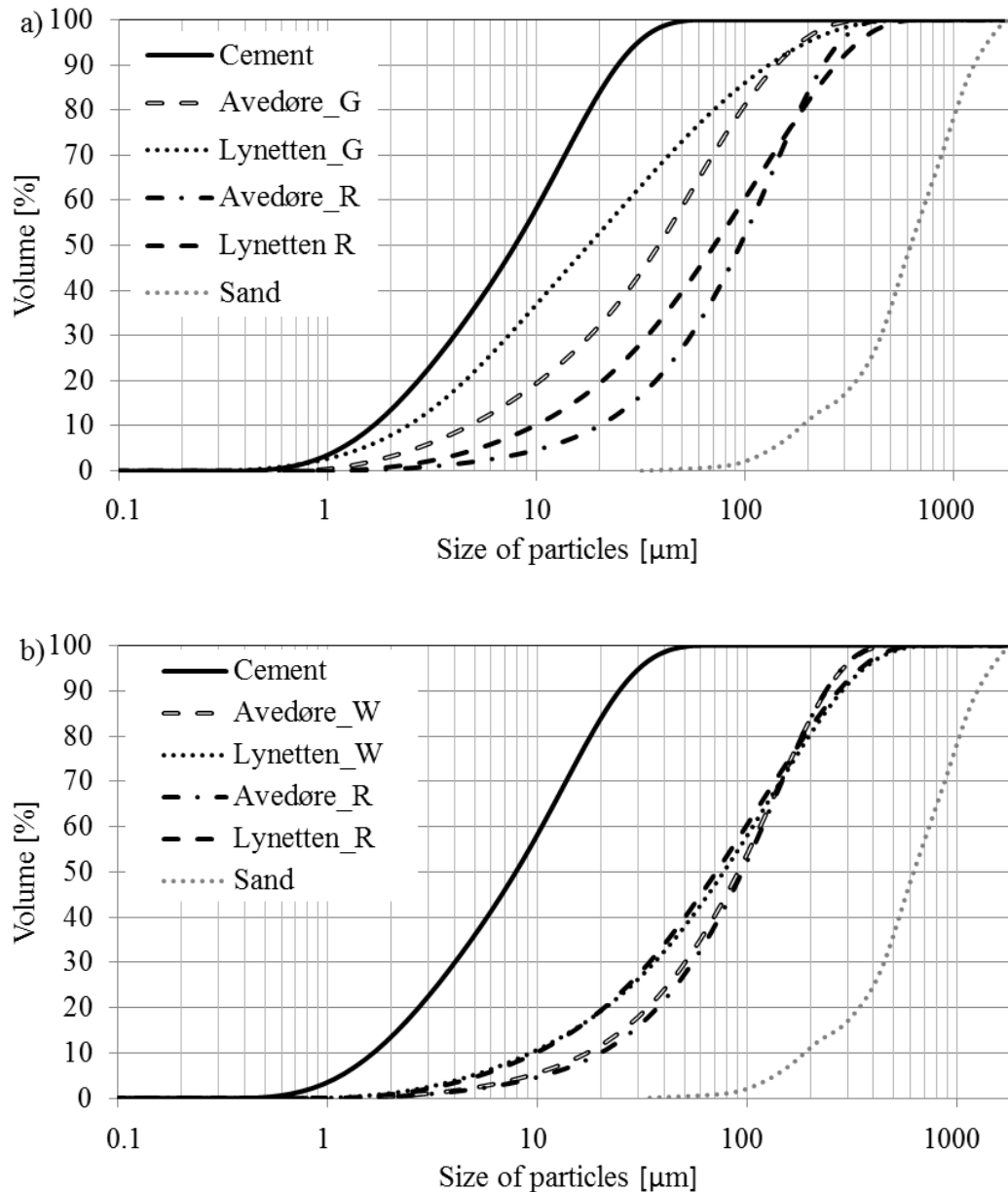


Figure 3.1 Particle size distribution – undersize curves; comparisons of Basis cement and SSAs. a) Cement, untreated (R) ash, ash ground (G) for 30 sec and sand b) Cement, untreated (R) ash, water-washed (W) ash and sand.

3.1.3 Open Porosity and Apparent Density of Mortar

The apparent density and open porosity of the different mortars (Table 3.2) indicate a minor influence of ash content on apparent density, while its influence on porosity was more obvious. The density slightly decreased (and the porosity increased) as the content of SSA increased, which may be because the SSA had a lower density than the cement and/or because of the irregular morphology of ash grains (Baeza-Brotons et al., 2014). The lowest porosity was observed for the REF mortar where only cement was present. Such a phenomenon is based on the fact that cement is reactive with water resulting in

more compact material and thus mortar made with cement and no ash had lower porosity. In general, a small effect of ash content on porosity was observed with 10% cement replacement by SSA (AVE10G, LYN10G) compared to REF. An increase in porosity by more than 20% was found for AVE30W compared to REF. The effect of ash grinding was visible at a replacement ratio of 30%, i.e. when comparing AVE30G with AVE30W. Thus, the porosity of the mortar with ground SSAs slightly decreased as the fineness of the SSA increased.

Table 3.2 Apparent density ρ_o and open porosity P_o including standard deviations (SD) and their relative changes.

Material	ρ_o [kg/m ³]	SD	Relative change [%]	P_o [%]	SD	Relative change [%]
REF	2107.1	24.0		16.5	1.2	
AVE10G	2081.2	27.8	-1.2	18.1	1.5	9.8
AVE10W	2081.3	35.6	-1.2	17.4	2.2	5.9
AVE30G	2071.5	14.7	-1.7	19.2	0.9	16.4
AVE30W	2043.2	8.3	-3.0	20.4	0.3	23.7
LYN10G	2079.5	26.9	-1.3	17.2	1.7	4.7
LYN10W	2078.5	27.2	-1.4	17.4	1.8	5.6
LYN30G	2063.4	13.8	-2.1	19.2	1.0	16.6

3.1.4 Compressive Strength

Compressive strength is one of the most important characteristics of a structural building material. This parameter was therefore included in the test schedule despite the large amount of published data on the subject.

Table 3.3 shows the compressive strength of the mortar samples after 28 days of curing. The compressive strength, in general, decreased with increasing ash content compared to the reference mortar. It has previously been studied that grinding of SSA may improve the ash quality with respect to its use as an SCM (Donatello et al., 2010b; Kappel et al., 2017; Ottosen et al., 2013a; Pan et al., 2003). The results obtained in this study support the previous findings (Ottosen et al., 2013a), in which increased compressive strength was reported for samples containing SSA that had been ground for 30 sec compared to SSA treated by water washing. A more evident effect was observed for 30% cement replacement by SSA, in terms of compressive strength loss.

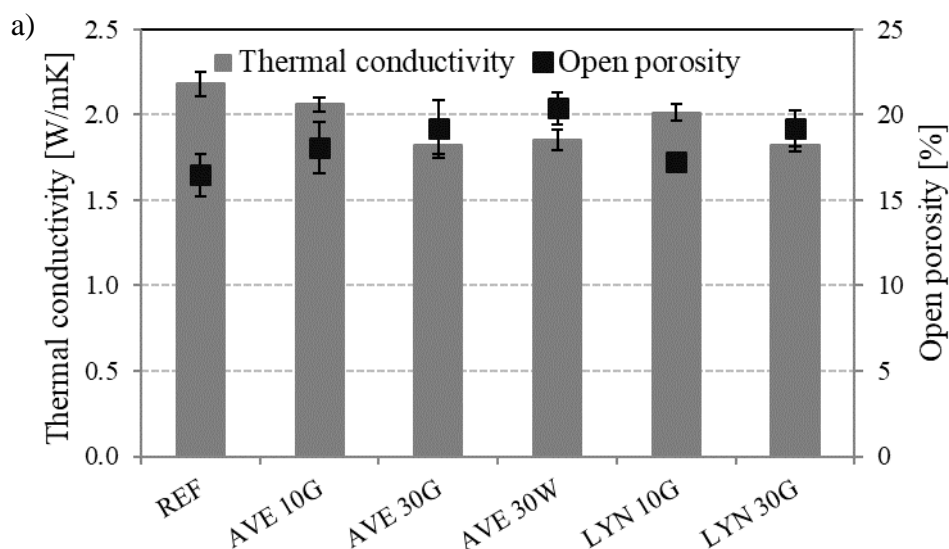
Table 3.3 28-day compressive strengths of mortar test specimens including standard deviations (SD) and their relative changes.

Cement replacement	Compressive strength [MPa]							
	0%	SD	10%	SD	Relative change [%]	30%	SD	Relative change [%]
REF	59.5	3.5						
AVE G			44.4	4.7	-25.4	39.4	1.0	-33.8
AVE W			44.8	2.5	-24.6	23.3	2.0	-60.8
LYN G			48.1	5.9	-19.1	37.6	2.1	-36.8
LYN W			45.6	3.5	-23.3	24.7	2.4	-58.5

3.2 Hygrothermal Assessment of Mortar

3.2.1 Thermal Conductivity with Relation to Open Porosity

Figure 3.2 a) shows the relation between the porosity and thermal conductivity, while Figure 3.2 b) reports on measured values of thermal conductivity. A coarser ash texture compared to the fine cement grains resulted in a higher porosity in the mortar containing ash compared to the REF. As expected, thermal conductivity increased with decreased porosity as the insulating ability of air is greater than that of the solid constituents of mortar. Specifically, the reference material with 0% ash has the highest thermal conductivity compared to the mortar containing ash.



b) Material	λ		Relative
	[W/mK]	SD	change [%]
REF	2.2	0.07	
AVE 10G	2.1	0.04	-5.5
AVE 30G	1.8	0.05	-16.5
AVE 30W	1.9	0.06	-15.1
LYN 10G	2.0	0.05	-7.8
LYN 30G	1.8	0.04	-16.5
LYN 30W	1.5	0.07	-29.4

Figure 3.2 a) Graphical relation of average values and standard deviations of three duplicates for thermal conductivity and porosity, b) Thermal conductivity including standard deviations (SD) and its relative change.

3.2.2 Water Vapour Adsorption Test of the Cement, SSAs and Mortar

The water vapour adsorption capability of cement, of ground and water washed SSAs and of mortar samples are shown in Figure 3.3. The graph clearly reveals that the moisture adsorption of cement is higher than that of the SSAs when exposed to identical conditions. It is evident that LYN ash adsorbed more moisture at all values of RH, both in the ground and water washed form, compared to AVE. This is linked to the finer particle sizes of LYN ash (Figure 3.1), which gives it a larger relative surface area and/or may be also related to the content of hygroscopic salts. While differences between the individual components are clearly visible based on a comparison of sorption curves for cement and SSA particles, the measurements of the mortars were not or only to a minimal extent affected by replacement of up to 30% of the cement content.

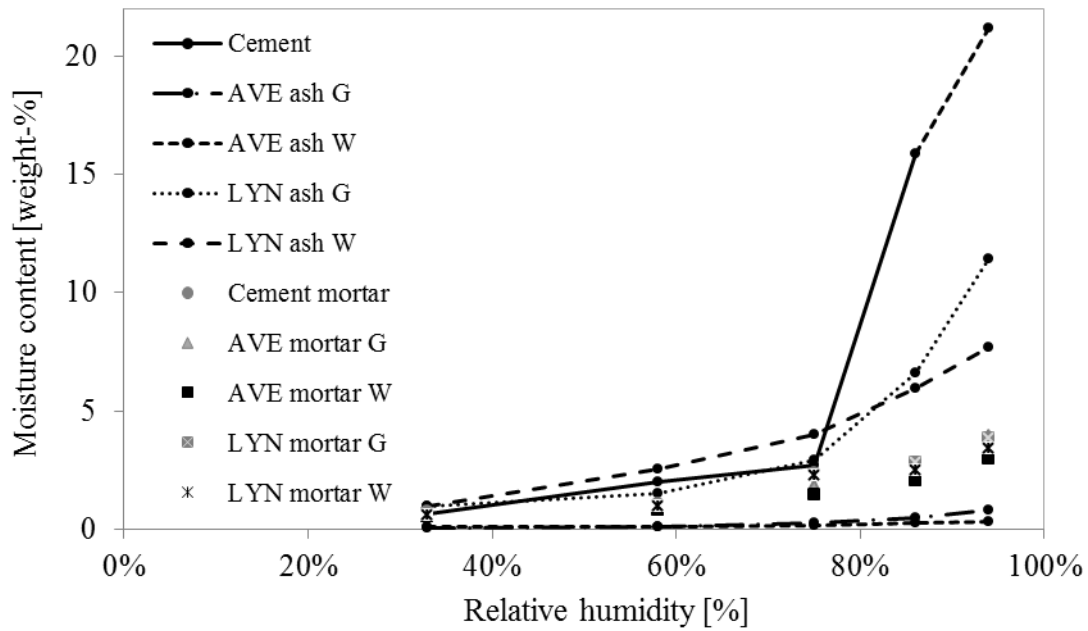


Figure 3.3 Sorption isotherms of the cement, treated SSAs, cement mortar and mortar with 30% treated SSA as SCM. (AVE – Avedøre ash, LYN – Lynetten ash, G – ground, W – water-washed). The sorption curve of cement did not reach equilibrium above 86% RH and the line is thus dashed.

3.2.3 Water Vapour Permeability

Measurements of the water vapour permeability are shown in Figure 3.4. Comparing the different mortar compositions, the water vapour permeability increased with the increased ash to cement ratio. An analysis of the results from the initial dry cup test and its repetition one year later showed a significant decrease in the water vapour permeability with the age of the cementitious material. Wet cup test was performed after first dry cup test and second dry cup test was performed one year later. The dry cup test was repeated based on the fact that initial permeability obtained from the dry cup test was higher than that from the wet cup test. Such observations suggested that modifications in microstructure occurred after the wet cup test.

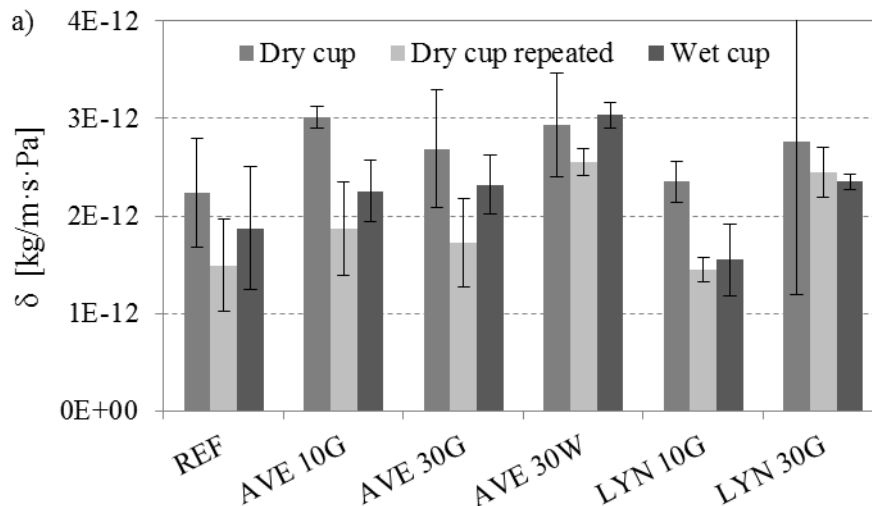


Figure 3.4 Average values of three duplicates for water vapour permeability δ [$\text{kg}/(\text{m}\cdot\text{s}\cdot\text{Pa})$] of the mortar samples and standard deviation (SD).

3.2.4 Capillary Absorption (Water Uptake)

The results of the capillary water absorption test are presented in Figure 3.5 in form of water absorption coefficients. The water absorption coefficient increased significantly with the increased ash to cement ratio, but it was not affected either by ash type or ash pre-treatment method. Mortars containing 30% SSA had water-absorption coefficients of about 2.5 times higher of the value for REF mortar.

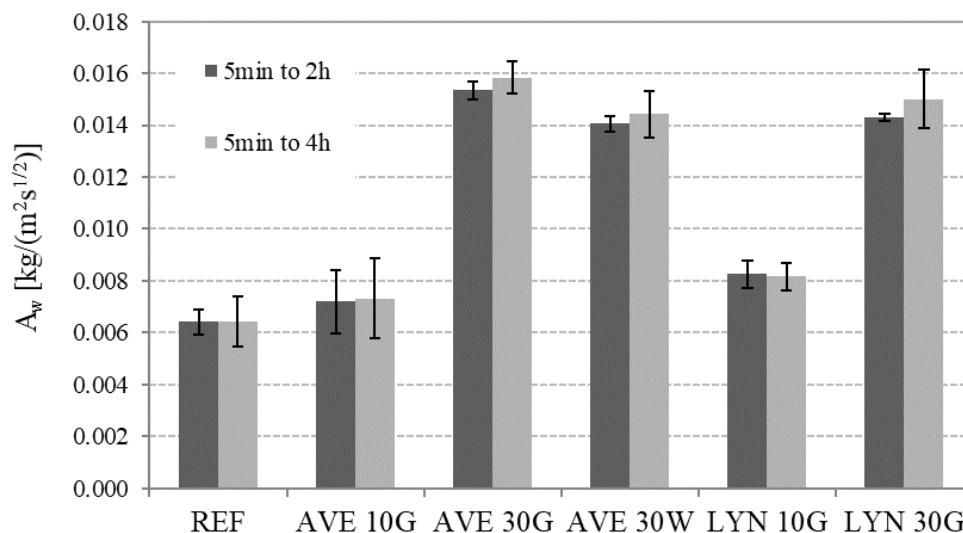


Figure 3.5 Water absorption coefficients (A_w) for mortars with different grades of SCM and their standard deviations. A_w was determined for two different time intervals.

3.2.5 Carbonation

Figure 3.6 shows the calcium carbonate content in newly-cast mortars (cured in water for 28 days, then dried and tested) that were prepared for the purpose of carbonation

test and had never been used in other tests (NEW I). Comparison of 'NEW I' and 'NEW II' shows that drying in the oven under 45 °C only slightly affected carbonate content. While exposure to air at 50% RH for 8 weeks (NEW III) had a clear impact on carbonation process of mortar.

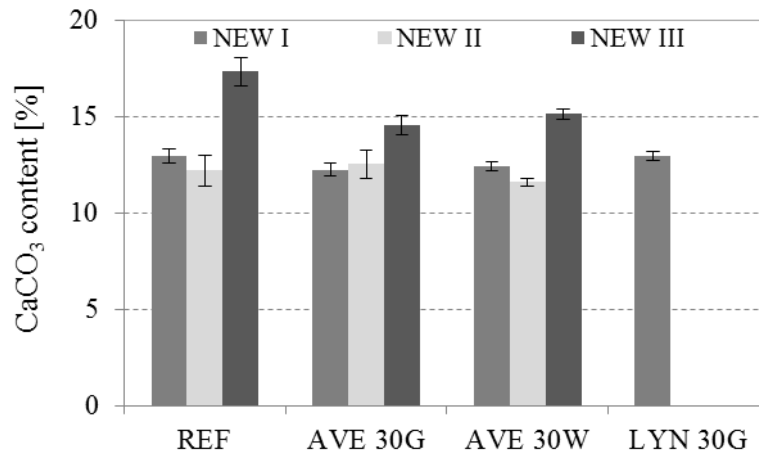


Figure 3.6 Results of the carbonation test shown as CaCO_3 content in mortar samples and their SD.

3.3 Impact of mortar on Indoor Air Quality and its Air Cleaning Potential

3.3.1 Sensory Assessments

Figure 3.7 shows mean odour intensity from perceived air quality assessments of the air extracted from the chambers containing cement-based mortar slabs (CM), cement-ash-based mortar slabs (AM), linoleum (Li), carpet (Ca) and their combinations (see Table 2.3 for loadings and set up). The upper parts of the diagrams (both a) and b)) of the Figure 3.7 show that when mortar slabs were present alone in the chambers, there was no significant difference in the mean odour intensity produced by either cement-based mortar or cement-ash-based mortar at the same loading. In the lower part of the diagrams, it is shown that the addition of linoleum or carpet to mortars at the lowest loading level of 1.4 m² significantly increased the odour intensity ($p < 0.05$). Increasing the loading of mortars with linoleum significantly decreased the perceived odour intensity ($p < 0.05$). Increasing the loading of mortars did not change the odour intensity in the case of the combination of carpet and the cement-ash-based mortar but significantly decreased the odour intensity when carpet and cement-based mortar were both present.

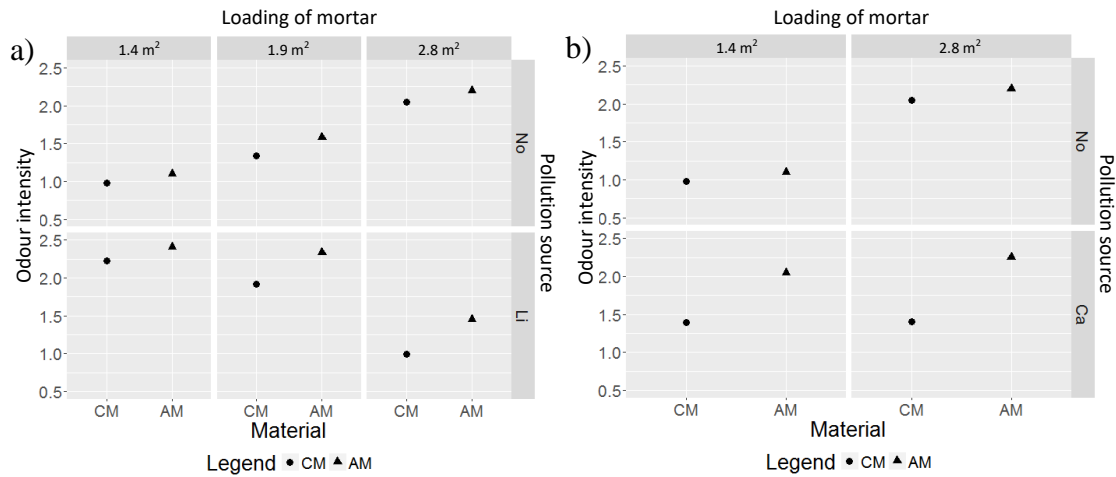


Figure 3.7 Interaction of the materials, loadings and pollution sources and their effect on odour intensity; a) odour intensity produced by mortar samples at different loadings when present alone and in combination with linoleum, b) odour intensity produced by mortar samples at different loadings when present alone and in combination with carpet. Materials: CM – cement-based mortar, AM – cement-ash-based mortar, Pollution source: No – no pollution source, Li – linoleum (only 1.4 m²), Ca – carpet (only 1.4 m²), Odour intensity: 0 – No odour, 1 – Slight odour, 2 – Moderate odour, 3 – Strong odour.

3.3.2 Chemical Measurements

Table 3.4 presents the results of the GC-MS analyses, listing the compounds detected with a toluene equivalent concentration higher than 1 µg/m³. It is shown that any differences in types and concentration of VOCs emitted by cement-based and cement-ash-based mortars were negligible. The only deviation was observed in a group of alcohols where highest concentration of 275 µg/m³ was detected for cement-based mortar at loading of 2.8 m². The reason for the difference was the high concentration of triethylene glycol (270 µg/m³). Neither of the mortar is expected to emit this compound and its presence was probably due to a residue of cleaning agent used to clean the glass chambers. In the case of linoleum, the measurements showed that it was a strong source of organic acids, many of which occurred at fairly high concentrations, often close to their odour thresholds. The results presented in the Table 3.4 show that the concentrations of these acids decreased when linoleum was present in combination with cement-based and cement-ash-based mortars. Carpet was proved to be a moderate source of acids, alcohols and aldehydes. When carpet was present in combination with the mortars, the concentration of acids decreased as in the case of linoleum and the concentrations of other compounds remained unchanged. The only concentration of specific alkanes was high when cement-based mortar was combined with carpet, compared to other conditions (sum alkanes 237 µg/m³). This can be explained by the fact that safe sampling volume was too low which was noted in the laboratory report. 4L sampling showed that the concentration of sum of alkanes under this condition was 4 µg/m³.

Table 3.4 Sums of concentrations of compounds emitted from the cement-based mortar (CM), cement-ash-based mortar (AM), linoleum (Li – only 1.4 m²), carpet (Ca – only 1.4 m²) and their combinations; the results are from the 3L samplings and the concentrations are toluene equivalents in µg/m³.

Materials	Concentration range µg/m ³ (3-litre sampling)								
	CM 2.8 m ²	AM 2.8 m ²	Linoleum (Li) 1.4 m ²	CM 1.4 m ² + Li	CM 2.8 m ² + Li	AM 2.8 m ² + Li	Carpet (Ca) 1.4 m ²	CM 2.8 m ² + Ca	AM 2.8 m ² + Ca
Sum Alcohols	275	17	8	9	4	4	17	13	4
Sum Aldehydes	2	6	17	10	8	14	22	19	9
Sum Organic Acids	15	9	290	21	41	19	131	26	50
Sum Alkanes	0	9	2	9	6	8	4	237	6
Sum other iso/cyclo-Alkanes:	129	152	4	138	94	110	38	84	95
Sum VVOC (< C6):	4	4	76	<1	4	<1	5	179	15
TVOC (C6-C16):	461	194	251	191	154	156	222	225	150
Sum SVOC (> C16):	< 1	< 1	<1	<1	<1	<1	<1	< 1	< 1
TVOC Toluene equivalents (ISO 16000-6):	243	90	42	120	36	62	199	81	46

Chapter 4

General Discussion and Implications

In the following, the results, implications and limitations of the study are discussed in the context of cement substitution by SSA in mortar production. As the cement industry belongs to one of the largest contributors to CO₂ emissions, the general aim is to find an alternative to cement in mortar/concrete production and thus help to reduce cement consumption where possible. Additionally, reusing of waste material, such as ash, would minimize the need of waste disposal, landfilling, mining raw materials and their related costs. This Ph.D. study was part of a larger research program studying possibilities of waste utilization in construction materials. This particular contribution aimed to investigate the effect of partial replacement of cement in mortar by SSA on mortar quality, its hygrothermal parameters and its impact on indoor air quality. These subjects are often not in the centre of an interest but they cannot be neglected when it comes to indoor environment quality and occupants' comfort.

4.1 Ash Characterization and its Effect on Mortar Quality

4.1.1 Chemical Characterization of SSA

The presence of certain chemical compounds in cement and ash affects many aspects of mortar casting (such as degree of hydration and its rate, workability), consequently mortar structure (porosity) and its compressive strength. Even when such compounds are present only in small amounts, they may measurably affect the resultant properties of the binder. Both ashes were proved to contain silicon dioxide (SiO₂), aluminium oxide (Al₂O₃) and iron oxide (Fe₂O₃) which are also major constituents of ordinary

cement and this provides a chance of a pozzolanic effect. If siliceous or siliceous-aluminous compounds are present in amorphous state, they can chemically react and form compounds possessing cementitious properties (Malhotra and Mehta, 1996). However, the content of reactive phase was not measured and the assessment of reactive content of SSAs is suggested for further investigations.

Another compound that directly affects reactivity of ash is phosphorus pentoxide (P_2O_5). The content of P_2O_5 was much higher in the SSAs compared to cement. A high content of P_2O_5 results in longer setting times and slow development of strength (Lin et al., 2009; Naamane et al., 2016; Nurse, 1952). Hewlett (2004) stated that if present in quantities of 1–2% in Portland cement clinker, it will slow down the hardening process. SSA added to cement instantly increases the total content of P_2O_5 in the mixture and thus may slow down the hardening process and reduce strength development of mortar. Although the hardening process was not assessed in this study, the decrease in 28-day compressive strength was observed for mortar containing SSA and it will be discussed in the following text.

4.1.2 Particle Size Distribution and Grain Morphology

Besides the chemical characteristics of ash, the particle size distribution and morphology of grains affect reactivity of cement-ash mixture i.e. the heat of hydration, the progress of hydration and consequently mortar porosity and its compressive strength (Frigione and Marra, 1976; Monzó et al., 1996). SSA is represented by irregular particles having a porous structure, which is probably related to the method of incineration (Bapat, 2012; Cyr et al., 2007). In the present study, the particle size range of the ashes was evidently larger than that of Basis Aalborg Portland cement. The particles of SSAs were about 10x coarser compared to cement grains. The coarser particles of ash resulted in modified mortar structure that influenced structure-related material properties, e.g. porosity, compressive strength, thermal conductivity, permeability, etc. Nevertheless, simply by grinding the ash for a specific period of time, a finer ash structure was achieved and a positive effect was observed on mechanical properties of mortar mixture compared to the water wash pre-treatment method. Water wash pre-treatment method had no effect on particle size distribution of SSAs since ash was decanted through a filter paper (11 μm) and thus measurable particles were not washed out. Additionally, cement had a narrower particle size distribution curve than the SSAs. This may affect the rate of hydration of the mortar mixture as well. The effect of SSA grain distribution on heat of hydration was studied by Chen and Poon (2017). They revealed that paste containing only SSA, and no cement, released no heat while pastes containing both cement and SSA reached higher peak of hydration rates than those pastes containing only cement. This is probably due to the porous structure of SSA that entraps water in its pores, leading to a higher concentration of cement particles in water, i.e. a lower effective water to cement ratio (Hu et al., 2014), that exceeds the dilution effect of the cement replaced by SSA (Lawrence et al., 2003).

4.1.3 Water Vapour Adsorption of SSAs and Cement

Another parameter studied was the sorption ability of SSAs and cement. By comparing the adsorption curves of the SSAs, it can be seen that each SSA has a different sorption capacity. The data clearly revealed that the moisture adsorption/hydration of cement is higher than that of the SSAs when exposed to identical conditions and the steepest increase of the adsorption curve was observed above 70% RH. Similar observations were reported in the previous studies (Patel et al., 1988; Powers, 1948; Wyrzykowski and Lura, 2016) where hydration of cement paste almost ceased under 80% RH. Comparing the different pre-treatment methods of SSAs, the ground SSAs had higher water vapour sorption capacity at the highest RH than the water washed samples as grinding increased the relative surface area of grains. In addition, another phenomenon was observed. Cement did not reach equilibrium for the conditions at 94% RH while the ashes did so at the set time period. This may be due to the reactions of the cement with water, which proceed slower when water is present in vapour state compared to water in liquid phase. This also implies that cement requires a long period of time to become fully hydrated (Nilsson, 1980), while SSA may not hydrate itself and only bonds with water in its pores (Chen and Poon, 2017).

4.1.4 Porosity and Compressive Strength of Mortar

Mortar is a porous solid, which by its nature has properties based on its constituents and their chemical reactivity. When a concentrated suspension of cement and ash in water is mixed, the reaction products are formed as a coherent matrix that encloses the residues of non-hydrated grains. The hydration process may take place over a long period, even after the set hardening period, and the matrix retains some of its porosity while hydration continues. It is anticipated that replacing cement by ash virtually affects chemical reactions of present constituents and consequently the mortar structure. The porosity of a material has a considerable influence on its mechanical properties in general. As porosity appears to be the main factor that determines the strength of cement-based material (Rößler and Odler, 1985), both of the parameters will be discussed simultaneously.

The increased amount of ash additive in mortar mixture increased the porosity of the mortar samples and thus adversely affected compressive strength. Principally, porosity increased and compressive strength decreased with increased ash to cement ratio. Porosity and density reflect the hydration state of the mortar and are directly related to each other, such that the increase of porosity is linked to the decrease of apparent density. This is a consequence of bigger and irregular grains of ash compared to cement, and higher porosity and lower apparent density of ash (Baeza-Brotons et al., 2014). In the present study, two different concepts were applied, i.e. different substitution ratios of cement and two ash pre-treatment methods. Regarding the earlier, porosity was highest when 30% of cement was replaced by water washed ash. Only a small effect of ash

content on porosity was observed when 10% of cement was replaced. Similar observations were recorded by Chen and Poon (2017), who explained it as a balance of the effect of higher ash porosity that improves hydration of cement by water entrapped in ash pores. For the latter, the ash pre-treatment method had a slight effect on mortar porosity at a replacement ratio of 30%. This was possible because ash grinding provided finer particles (Donatello et al., 2010a; Kappel et al., 2017) compared to the water wash method, which did not affect grain size distribution.

As outlined above, mortar strength is affected by the presence of major and minor components, the specific surface area, particle size distribution and grain morphology (Lawrence, 1998). The compressive strength, in general, decreased with the decreased cement to ash ratio together with the increased water to cement ratio (the dilution effect). This may be a consequence of irregular particles of SSA, which may retain water, and/or high content of P_2O_5 in SSA, which result in decreased workability, longer setting time, delay of hydration (Lawrence, 1998; Piasta and Lukawska, 2016) and subsequently in compressive strength drop (Nurse, 1952). P_2O_5 forms a matrix, while consuming the water, with the reactive CaO and SiO_2 reducing their availability for pozzolanic reactions. On the other hand, irregularly shaped SSA particles may enhance the interlocking among grains of ash and cement and may serve as a place to accommodate hydration products and thus consequently support overall strength. However, this was not investigated any further. Additionally, grinded ash used in the mortar mixture resulted in improved compressive strength (decreased porosity) compared to the water washed ash. Such results were more evident for higher percentage of the ash incorporated in the mortar mixture. These findings support previous studies discussing the effect of SSA grinding on mortar quality (Donatello et al., 2010b; Kappel et al., 2017; Ottosen et al., 2013a; Pan et al., 2003). Despite the decreased compressive strength of cement-ash-based mortar, mortar with high cement replacement ratio can still find its application, e.g. as a final, non-loadbearing layer of the facade.

4.2 Hygrothermal Assessment of Mortar

4.2.1 Thermal Conductivity

Results on thermal conductivity revealed that a decrease in thermal conductivity correlates with an increase in porosity. Specifically, thermal conductivity of mortar was reduced by 15–16.5% on average when 30% of cement was replaced by SSA. This complies with the fact that pores filled with air play the function as insulation. Such an effect of ash content may positively reflect itself in a reduced thermal transmittance of the wall structure. In a case of mortar application as a completing layer on the wall, this specific layer is rather thin. On the contrary, considering mortar mixture as a part of the concrete, it is mostly the aggregate that influences the final thermal conductivity of the material.

4.2.2 Water Vapour Adsorption Tests

In order to determine hygroscopic water content in the material, knowledge of sorption isotherm of a material is required. In this study, sorptivity tests were performed using two different methods, i.e. climatic chamber and sealed glass containers (desiccators). The earlier, climatic chamber method was represented by transparent chamber where relative humidity was kept constant by supplied air of specific relative humidity. No CO₂ filter was installed in the system, thus the CO₂ level inside the chamber was related to the CO₂ concentration in the supplied air. The latter method involved sealed glass desiccators where air volume was exchanged only during weighing process. Thus, the climatic chamber method imitates more credibly the real environment where materials are permanently exposed to air containing CO₂. However, the weakness of the climatic chamber method is that the effect of CO₂ on small samples with few mm in diameter is rapid and more evident compared to the massive building structure. On the contrary, the advantage of the desiccator method lies in the fact that various measurement steps, i.e. different relative humidity steps, can be performed simultaneously. The measurements can be processed faster than using climatic chamber and at the same time the natural aging effect is approximately the same for all the studied samples. The comparison of both tests revealed that slightly higher mass difference was observed when the climatic chamber method was applied compared to the desiccator method. Clear differences between mortar mixtures were reported from the test performed in the climatic chamber, specifically for relative humidity higher than 50%. The amount of water vapour adsorbed was highest for the cement-based mortar. In general, with decreased cement to ash ratio the ability to adsorb water vapour decreased. No clear effect of ash pre-treatment was observed. Such findings corroborate with the previously discussed results on sorption isotherms of individual constituents, i.e. the SSAs and cement. This indicates that sorption ability of the samples may be affected by the potential reactivity of cement/ash with water, which was clearly higher for cement. Another factor affecting sorption curves is carbonation process due to the presence of CO₂, which contributes to increase of mass of the samples (Neville, 2011). On the contrary to these observations, sorption isotherms obtained from desiccators coincided with each other independently of the mortar composition. Comparison of both methods reveals that the method applied may affect measured parameters to such an extent that the reported results may slightly differ. The assessment procedure of hygroscopic properties of cementitious materials is not clearly defined in a standard and it is not easy to evaluate the outcome considering that it can be easily affected by capillary effects between condensation and evaporation in the pores, the chemical water uptake, drying process, repeated cycles, carbonation and chemical aging. Therefore, it is recommended that a chosen test method is suitable for sorption isotherm determination of cementitious materials and it should be contemplated based on the purpose of the study.

4.2.3 Water Vapour Permeability and Capillary Absorption

The transfer of water vapour and liquid water in a porous material relate to its pore distribution and tortuosity. With respect to capillary suction, the water uptake coefficient rapidly increased with increasing open porosity, however, it was not affected either by ash type nor by the ash pre-treatment method. This may indicate that mortar containing SSA, i.e. with higher porosity, has more pores in the capillary range than cement-based mortar. Similar observations were made for water vapour permeability, which clearly increased with decreased cement to ash ratio. Moreover, it can be concluded that grinding of the ash has an effect on open porosity of the mortar, i.e. finer ash grains result in lower porosity of mortar, and consequently can decrease permeability of the material compared to the water wash pre-treatment.

4.2.4 Carbonation

Several processes have significant effect on the structure of cementitious materials, e.g. hydration of cement (Lawrence, 1998), drying process (Beaudoin and Tamtsia, 2004), chemical aging (Thomas and Jennings, 2006) and carbonation (Johannesson and Utgenannt, 2001). It could be expected that such processes affect material parameters and its behaviour. Espinosa and Franke (2006b) defined two kinds of time-dependent processes that take place simultaneously during exposition to real climate/weathering, i.e. carbonation and chemical aging. They reported that both processes affect the pore structure and also the sorption behaviour. Carbonation leads to a strong reduction of the pore volume and generally to a substantial reduction of water uptake. Structural modifications of mortar related to carbonation process were also described by Pham (2013). He reported that micropores were clogged, and thus microporosity decreased, while distribution of mesopores increased to the detriment of volume of micropores. A chemical aging process also causes a change of the microstructure of the hardened cement paste. It proceeds gradually causing a completely irreversible change of the pore structure due to the compression of the cement gel particles (Espinosa and Franke, 2006b). The present study focused only on the carbonation effect. The aim was to track the changes in material properties due to ash content rather than investigating aging effect of cement particles. The detailed description of time-dependent processes and their effect on mortar structure with respect to mortar composition and potential cement substitutes are proposed for further research.

Basically, carbonation is a natural process occurring in moist environments with access to CO_2 , and it produces carbonate product (CaCO_3). This reaction results in mass increase of samples based on a simple molar mass calculation. The initial CaCO_3 content in newly cast mortar was almost equal for all the samples without any specific differences between mortar mixtures, and thus the effect of 30% replacement of cement by SSAs did not make any difference. It is worth to note that a part of CaCO_3 content

probably came from limestone in Portland cement used in mortar mixtures. After exposure to supplied air (50% RH and atmospheric CO₂) in a climatic chamber for 8 weeks, the content of CaCO₃ increased rapidly from 12.9% to 17.3% for cement-based mortar and from 12.2% to 14.6% for cement-ash-based mortar containing 30% of ground Avedøre ash (Figure 3.6). Chemical analyses on major oxide content reported that cement and both SSAs contained calcium oxide (CaO). Then the product of hydration, specifically Ca(OH)₂, may then react with carbonic acid (as CO₂ is not reactive itself (Neville, 2011) producing CaCO₃. Nevertheless, the amount of CaO was not the same in the individual constituents. The CaO content was almost triple for cement compared to ash from Avedøre plant indicating that production of CaCO₃ is higher for cement-based samples. However, as noted before, the content of reactive phase was not measured for any constituent. The reported findings imply that modifications in mortar due to carbonation can take place rather fast especially considering samples with small diameter. Consequently, some of mortar characteristics may be significantly affected. For example, the process of carbonation increases the mass of the cement paste. CO₂ is fixed by the hydrated cement paste (Neville, 2011) and increases the mass of the sample as it was observed in a case of sorption isotherms where two methods with and without free CO₂ access were applied. In a case of vapour permeability test, first dry cup test provided higher permeability compared to the later repeated dry cup test. This is because CaCO₃ occupies a greater volume than Ca(OH)₂ which it replaces and the porosity of carbonated mortar is reduced (Neville, 2011). Yet, to confirm such assumptions, no examination of pore size distribution was performed. Some observations of carbonation effect on mortar structure modifications and related material properties were reported in the literature (Espinosa and Franke, 2006a, 2006b; Issaadi et al., 2015; Pham, 2013, 2014a, 2014d; Saeidpour and Wadsö, 2016; Šavija and Luković, 2016).

4.3 Impact of mortar on Indoor Air Quality and its Air Cleaning Potential

4.3.1 Emissions and Odours from Mortar samples

Only the ratings of odour intensity are discussed here because relative humidity was not controlled in the steel chambers and this could bias the assessments of acceptability of air quality (Fang et al., 1998). On the other hand, perception of odour intensity is not affected by varying temperature and relative humidity of the inhaled air (Fang et al., 1998). Two aspects of material behaviour were considered with respect to produced odour, specifically materials acting as a sink and/or as a source of emissions. In order to assess mortar interaction with pollutants typically present indoors, two pollutant sources such as linoleum and carpet (Gunnarsen et al., 1994; Jensen et al., 1995b, 1995a; Johnsen et al., 1991; Wargocki, 1998; Wargocki et al., 1999; Wolkoff et al.,

1993) were studied under conditions when present alone and in combination with mortar. The emissions were examined by two measures i.e. performing the sensory and the chemical analyses.

Sensory assessment of odour intensity did not indicate differences in emissions between cement-based mortar and cement-ash-based mortar. Mortar samples were mostly composed of inorganic components, which were not measured in the present experiment. Based on the chemical measurements, they were mostly sources of iso/cyclo-alkanes. As mentioned in the Green Concrete study (Bødker, 2006a), the mineral oil sprayed into the mould used to cast mortar slabs may be responsible for emissions of such hydrocarbons, a functional group of compounds containing alkanes, cycloalkanes and others. Overall, it may be concluded that replacing cement by SSA in the mortar did not have an effect on PAQ and measurable part of emissions based on both sensory perception and chemical analyses.

4.3.2 Interaction of Emissions from Mortar, Linoleum, Carpet and Air Cleaning Potential

The odour intensity increased when linoleum was placed together with mortar samples at the lowest loading level of 1.4 m² in the glass chambers, as linoleum alone represented a source of strong odour. However, the odour intensity decreased when the loading of the mortars was increased. It reached even lower level than that of cement-based mortar alone. The observed phenomenon can be explained by absorption of the pollutants emitted from the linoleum. In particular, linoleum was detected as a strong source of organic acids, while the mortar generally represents a strong base, especially when freshly cast, fresh mortar has high pH approx. 13 (Neville, 2011). It is mainly organic acids that possess low odour threshold thus can be detected by human nose and can cause irritation (“CDC - The National Institute for Occupational Safety and Health (NIOSH),” n.d.). As a consequence of acids being attracted by basic environment, the odour originating from acids can be neutralized. Such sink effect was seen both for the cement-based and cement-ash-based mortar suggesting that addition of SSA did not change the sorption properties. It is recommended to focus on the potential for adsorbing organic acids in time in future studies. Additionally, it is possible that adsorption was not the only mechanism responsible for odour reduction. Possibly, odour produced by the mortars might mask odour from linoleum, or pollutants may block the pores on the material surfaces and thus prevent surface in pores from emitting. Another explanation of the observed phenomenon can be the compensation/subtraction of odour intensities (i.e. the mixture smells weaker than both the stronger and the weaker components alone), which was described by Cain and Drexler (1974). Examination and elucidation of these processes are worth further studies.

Concerning the carpet and its assessment, carpet alone provided slightly higher than moderate odour intensity. Chemical measurements revealed that carpet was a moderate-

to-low source of organic acids, aldehydes and alcohols. When carpet and mortar were studied together, a reduction in concentrations in some compound groups was reported i.e. reduction of alcohols, aldehydes and organic acids. However, the extent of odour reduction was not comparable to the one observed in the case of combined exposure of linoleum and mortars. Lower concentration of organic acids detected from the carpet can explain why the sink effect was much smaller.

Such observations were not identified in other studies and provided a distinctive perspective to mortar potential. The only study on impact of sorption on PAQ was performed by Sakr et al. (2006) but with gypsum boards. Observed behaviour indicates air-cleaning ability of mortar that may contribute to improved air quality indoors and/or reduced ventilation rates necessary for pollution removal. It is also important to highlight the consistency of sensory assessment trends that show repeated tendency for cement-based and cement-ash-based mortar and their interaction with linoleum and carpet.

4.3.3 TVOC as General Indicator of Indoor Air Quality

Another interesting finding was related to the measured TVOC concentrations. While the strongest odour among all tested conditions was produced by linoleum, the highest TVOC concentration was detected for the cement-based mortar. The reason for the highest TVOC level was the high concentration of triethylene glycol, which was probably due to the presence of residues of cleaning detergent used for the cleaning of the glass chambers. Taking these results into account it can be concluded that pure chemical measurements may not always provide correct information on the potential effect of material emissions on perceived air quality. The known TVOC concentration alone may not be able to predict the effect on humans (Andersen et al., 1996). It has been also shown that detailed analysis of pollutants was worthwhile because a clear difference between the concentrations of individual pollutants and the sum of concentrations of functional groups was observed.

4.4 Practical Implications

- Partial cement replacement by SSA in mortar production seems to be, in general, a viable option to reduce both the negative impact of cement production on the environment and problems with ash disposal. It has been shown that replacement of cement by SSA of up to 10% does not or only to a minimal extent affect hygrothermal qualities of mortar and it can be a good compromise between mortar's environmental impact and material quality. Considering an actual application of mortar containing SSA, small changes of mortar characteristics do not have to possess any limitations of cement-ash-based mortar administration. For example: application in a completing layer on the wall construction.

- Although the mortar structure gets affected by bigger ash particles compared to cement, simple ash grinding can positively affect specific parameters of mortar, e.g. porosity and compressive strength.
- Increased ash to cement ratio resulted in decreased thermal conductivity and hygroscopicity, while water vapour permeability and absorption coefficient increased. These modifications can, however, be beneficially used in particular situations, e.g. in a case when water vapour sorption is not desired or when more permeable material is needed.
- An ash content of 30% reduced the thermal conductivity by approx. 15% compared to the cement-based mortar. This may improve the insulating performance of the whole construction depending on the mortar application and consequently save energy used for heating.
- Information on TVOC alone may not provide sufficient knowledge on emissions released from building products. It is suggested to differentiate between functional groups of pollutants rather than reporting total concentrations of VOCs.
- A cement-ash-based mortar is not a source of a higher odour load compared to a pure cement-based mortar. With respect to odour perception, cement-ash-based mortar slabs can safely be applied.
- Both cement-based and cement-ash-based mortars possess an ability to reduce odours, especially in a case when organic acids are the sources of odour. Potentially, this phenomenon can itself be considered as an air-cleaning mechanism or as an incentive for manufacturing of air-cleaning materials.

4.5 Limitations

- The inherent variability of SSA composition remains one of the reasons for avoiding a systematic generalization of its application.
- The specific cement used in the mortars studied in this work was Basis Aalborg cement. Basis Aalborg cement is a Portland-composite cement classified as CEM II/A-LL with a variable content of limestone, specifically within the range 6–20%. This type of cement was used based on its common application in practise, and as it partly contains a raw material (limestone) instead of processed cement. However, the producer does not ensure a constant content of limestone and thus its content may vary between different batches. The cement used for mortar casting may vary slightly in composition and that hinders comparison of samples containing cement coming from different batches.
- Several processes have a significant effect on structure and quality of cementitious materials, such as the continuous hydration of cement, aging, drying, carbonation etc. They depend on the following factors: age of the samples, moisture and thermal conditions and access of CO₂ while stored. Samples used in the

different experiments were of slightly divergent age, which leads to some inconsistency of the study. Consistency of the composition of samples, their age and method of storage is recommended to be kept under control during the whole period of study.

- Examination of materials under laboratory conditions provides fundamental knowledge on material behaviour but the assessment of an authentic scenario is recommended to be performed separately.
- In the study on sensory ratings of emissions, participating respondents were not typical representatives of a population. Their educational status was higher than average, as they were all university students. Also their age of 22–38 is not representing average age. Moreover, perception of odours may be influenced by age, health condition and socio-economical background of the respondent.
- The chemical assessment of emissions was performed a year after the sensory assessment. Although materials were stored wrapped, some changes in emission rates may be anticipated.

4.6 Recommendations for Future Work

- It is suggested to apply various SSAs from different sources in mortar and compare their effects on hygrothermal performance of mortar and PAQ.
- Different pre-treatment methods of SSA can be applied to modify SSA's effect on mortar quality, e.g. water wash, acid wash and grinding. Especially the effect of grinding method, that showed potential of improving mortar quality, should be investigated with respect to different grinding time intervals.
- Detailed description of time-dependent processes and their effect on mortar structure with respect to mortar composition and potential cement substitutes is proposed for further research. Such knowledge would enable a comprehensive estimation of modifications in hygrothermal performance (thermal conductivity, sorption, permeability) of mortars and an interaction between material and the adjacent environment (to study source and sink effects).
- It is proposed to investigate the effect of the grain size distribution and morphology of SSAs after different pre-treatments (water wash, acid wash, grinding) on the hydration process.
- Standard procedures and conditions of hygrothermal assessment of cementitious materials should be clearly delineated. The structure of cementitious materials gets easily affected by the thermal and moisture conditions, CO₂ concentrations and, in general, by the environment they are exposed to. Comprehensive guidelines for investigations of cementitious materials would facilitate correlations of findings from different sources/authors.
- It is recommended to state the energy implications of substitution of cement by SSA based on hygrothermal behaviour of cement-based mortar versus cement-ash-based mortar.

- Evaluations of the actual and the long-term capacity of the mortar (the effect of aging) for sorption of water vapour, organic acids and other pollutants would help to clarify the air-cleaning potential of mortar. Long-term measurements would contribute to better understanding of mechanisms responsible for odour reduction, moisture and pollution buffering.
- The effect of different conditions, specifically the effect of temperature and relative humidity on emissions released from material surfaces and on material sorption ability, is suggested for future investigation. Every reaction on material surface is unique and needs its optimum conditions in order to take place.
- Examination of the processes responsible for the compensation effect of odour intensities that was observed in the sensory experiment when the combination of mortar with linoleum was investigated. Mechanism of odour compensation of mortar needs to be further studied. Understanding the mechanism of odour compensation, when different materials interact with each other, will be of benefit for design and manufacturing of so-called air-cleaning materials.
- Validation of the sensory findings in real scenarios is anticipated as next step. Small scale measurements under laboratory conditions do not represent typical conditions in real buildings.
- Standard regulations on compulsory testing of building materials are recommended to be specified together with obligatory limits and requirements. Manufacturers mostly test materials on parameters of their own interest.

Chapter 5

Conclusions

The study was carried out to investigate the potential use of SSA obtained as an incinerated by-product in sewage sludge treatment, as a possible supplementary cementitious material.

Generally, it can be concluded that the partial replacement of cement by SSA has an effect on the hygrothermal properties of mortar, especially those properties directly related to mortar structure (i.e. porosity) and at higher cement replacement ratios (i.e. 30%). With respect to sensory assessment, cement-ash-based mortar does not represent additional odour load compared to cement-based mortar at the same loading even when 30% of cement was replaced by SSA. Moreover, both mortars showed a potential as air-cleaning material. Based on the findings presented in the thesis, cement replacement by up to 10% in the mortar can be a good compromise of slightly modified mortar properties and a beneficial contribution to reduction of CO₂ emissions related to decreased cement consumption. At the same time, a need for ash landfilling can be reduced or even avoided which would improve ecological impact of sewage sludge incineration.

The primary part was devoted to basic characterization of SSAs and cement, and mortar components' effect on selected physical properties of mortar. These investigations confirmed previous findings concluding that composition of SSA is highly variable and even its origin from wastewater treatment plants located in the nearby areas does not ensure comparable quality. In particular, both ashes contained silicon dioxide (SiO₂), aluminium oxide (Al₂O₃) and iron oxide (Fe₂O₃) similarly to cement. Content of silica

in a reactive form was not measured, this is, however, a suggestion for future investigations. In addition, a high content of phosphorus pentoxide (P_2O_5) was detected, which may adversely affect the mortar setting and hardening process.

Particle size distribution indicated that particles of SSAs were characterized by larger grains compared to cement. The open porosity of the mortar was clearly affected by larger particle size and different morphology of ash grains and so was the compressive strength. The mortar with the highest ash to cement ratio was the most porous and resulted in lower compressive strength compared to cement-based mortar. Similarly, the capillary water absorption coefficient increased in mortars with SSA. These properties may, however, be improved by simple ash grinding as a pre-treatment method providing finer particle sizes. On the contrary, water wash pre-treatment did not have any visible effect on particle size distribution of ash.

Another perspective compared the sorption abilities of cement and SSAs and their effect on sorption isotherms of mortar samples. Although significant differences were recognized in sorption isotherms of individual components, i.e. cement and ashes, their effect on sorption isotherms of mortars was minor (comparing sorption isotherms determined by the same method applied). The sorption isotherms of mortar with and without ash added were determined as well, this time using two different methods with free and limited access of CO_2 . It can be concluded that the sorption ability of mortars were not significantly affected by the sorption properties of cement and SSAs, yet some variations between isotherms were reported when different testing methods were applied.

Higher porosity of mortar, when cement was partly replaced by SSAs, had also effect on other parameters. Increased ash content yielded higher open porosity and resulted in decreased thermal conductivity and increased water vapour permeability. With 30% cement replacement, a reduction of 15% of thermal conductivity was measured. Depending on mortar application, this may positively contribute to energy savings and carbon footprint of building constructions.

The other part of the project looked at the effect of natural moist climate on mortar. Principally, mortar reacts with moisture and CO_2 , which is naturally present in air, resulting in changes of mortar microstructure. In order to investigate such effects, a test on calcium carbonate ($CaCO_3$) content was performed. Although the presence of calcium oxide (CaO) was proved for cement and both SSAs, $CaCO_3$ content was higher for cement-based mortar than for cement-ash-based mortar. Such findings indicate possible modifications in mortar composition due to the carbonation process and, in general, sensitivity of the studied material to applied methods. These should be carefully considered in the experimental setups and procedures, time planning of experiments as well as in data analyses.

The latest part of the study on mortars' emissions revealed that ash did not cause any significant difference between chemical emissions from cement-based and cement-ash-based mortar slabs, confirmed by both sensory and chemical assessments. The odour

intensity increased with the increased loadings of both cement-based and cement-ash-based mortar. Based on chemical measurements, mortar slabs were detected as strong sources of iso/cyclo alkanes, while linoleum and carpet were mainly sources of organic acids. Additionally, carpet was also linked to alcohol and aldehyde emissions.

Mortars (both w/ and w/o ash) were proved to be strong sinks especially for organic acids, which were emitted in fairly large amounts especially from linoleum and possess low odour threshold levels that can be detected by olfactory system. Such observations complied with the sensory assessment. The odour intensity of mortar together with linoleum was lower than the odour intensity of any of them when present alone. The sink effect was much smaller in the case of the combined exposure of mortars with carpet. Moreover, the sink effect was seen both for cement-based and cement-ash-based mortar. Such findings indicate a potential in odour/emission reduction by means of mortar applications. Thus, building materials should not only be considered as pollution sources, but also, in some cases, as potential air-cleaners.

Sensory assessment of material emissions was performed together with specific chemical analyses for identification of their potential effect on air quality. Observed decrease in concentrations of specific groups of compounds, especially organic acids, complied with the decrease in odour strength. Additionally, TVOC is not a good indicator of the sensory effects of emissions from materials, but the sums of functional groups of VOCs may be able to predict the effects on human perception.

Lastly, the reported findings can be handled as essential information for further investigations and critical assessment of SSA utilization in mortar/concrete production or as a reference to testing of alternative cementitious materials. They can be of benefit for cement/concrete manufacturers, material and indoor environment experts and principally can contribute to development of waste-based and concurrently low/non-polluting or even air-cleaning materials.

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Appendix

Paper I

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Characterization of sewage sludge ash and its effect on moisture physics of mortar



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ABSTRACT

A study was carried out to investigate the potential use of ash obtained as an incinerated by-product in sewage sludge treatment, as a possible supplementary cementitious material. Chemical parameters and granulometry of the sewage sludge ash and selected physical and hygroscopic properties of cement-ash-based mortar are presented and compared with results from previous studies. The effect of different ratios of cement substitution and two pre-treatment methods for ash, i.e. ash grinding and water washing, on the physical properties of mortar were investigated by using density, porosity and compressive strength as elemental indicators of the mortar quality. The hygroscopic sorption properties of the individual constituents alone and the resulting mortar samples were described by sorption isotherms for water vapour and by a capillary water absorption test. Results showed that the SSAs typically consisted of larger particles compared to the cement particles. Incorporation of ash resulted in more porous mortar structures compared to cement-based mortar, which affected the material's mechanical properties such as the compressive strength. 28-day compressive strength decreased with increasing ash content and porosity. Cement conveyed the greatest ability to adsorb and react with water and there were clear differences between the different ashes. Despite the differences in sorption properties between the different constituents, the effect of ash content on mortar sorption isotherms was negligible.

1. Introduction

Cement production is among the largest contributors to CO₂-emission caused by human activity. About 5–7% of global CO₂ emissions are from cement plants, and 900 kg CO₂ are emitted to the atmosphere during the production of one metric ton of cement [3]. Cement is mostly used as a binder in concrete. The CO₂ emission related to the making of concrete, including cement production, is between 0.1 and 0.2 t per ton of produced concrete [21]. With an annual global concrete production of approximately 3.8 billion cubic meters, concrete is the second most consumed material in the world, after water [54]. Even if only a small percentage of the overall use of cement could be substituted by alternative hydraulic binders, it would have a huge positive effect on the environmental impact of concrete production. With the vast use of Portland cement, concrete production has a significant carbon-footprint and currently represents 5% of the total global energy use in industry [61].

The use of industrial by-products (waste material) as alternatives to cement in concrete production reduces the need for landfilling and

related costs, and will consequently reduce the need to mine virgin raw materials. When secondary resources are used as partial replacements for cement, the generic term used for these products is “Supplementary Cementitious Material” (SCM) [57]. The main SCMs include coal fly ash, ground granulated blast furnace slag, silica fume, volcanic ash and metakaolin. Since the 1990s, fly ash from coal combustion processes has widely been used as an SCM. However, many countries are starting to use other raw sources of energy that are more sustainable than coal [33,58,8]. This means that there is increased interest in identifying other ashes that can be used as an SCM, instead of fly ash from coal.

Alternatives to cement should be based on a high abundance of raw material, low carbon emission, low energy consumption, low pollutant load and possible use of waste products. Clean production, use of recycled products, and cement substitution are three effective approaches for the sustainable development of the concrete industry [55]. One type of fly ash, which has shown potential as an SCM is Sewage Sludge Ash (SSA) [11,38,40,41,5,6,64].

Sewage sludge is a by-product formed during wastewater treatment. Approximately 10 Mt/year of dry mass sewage sludge is produced in

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European countries. However, incineration can reduce this amount by 70% by mass, and 90% by volume [19]. Sewage sludge has been widely used in agriculture as a fertilizer because of its content of phosphorus. However, in recent years the tendency has been to incinerate it. In the incineration process, the organic matter is combusted while by-products such as CO₂, trace gases and water vapour are produced. Also, that the process of waste disposal is not completed by incineration as the SSA contains a remarkable amount of residual unburnt material. It is estimated that the global production of SSA is approximately 1.7 million tons annually, mainly from the USA, the EU and Japan, and it is expected to increase [42,9]. A vast amount of SSA is currently being landfilled. Most SSAs are classified as waste, but it could also be regarded as a resource. Previous research has shown different options for the use of SSA in different construction materials: mortar, concrete, fired clay brick or lightweight foam materials [1,23,32,36,38,40,41,56,59,6,60,64]. Many of the applications simply use SSA as a direct substitute for raw materials such as clay or sand. However, most of these studies focused on the possibility of using SSA as an SCM in blended cement, due to the considerable environmental benefits that would be achieved.

There have been studies of several different aspects of the use of SSA as an SCM. A recent systematic review by Lynn et al. [38] covered selected physical and chemical characteristics of SSA and its use. The present paper adds to this knowledge by reporting the properties of both SSA itself and of hardened mortar containing SSA in terms of how they affect material moisture physics, including their water vapour sorption and capillary water uptake. The aim is to raise broader perspective on SSA used in mortar, its characterization (e.g. chemical composition, grains size distribution) and to relate the effect of SSA content on actual modifications in mortar structure and performance.

2. Materials and methods

2.1. Origin of the incinerated sewage sludge ashes

SSAs from the two major Danish mono-incineration plants were used. The sludge incinerated at both plants originated from municipal wastewater treatment. The SSAs were from Avedøre Wastewater treatment plant (AVE) and from Lynettefællesskabet (LYN) (Fig. 1a) and b) respectively). Both plants are located in Denmark, close to the capital Copenhagen. The two plants treat the wastewater coming from 17 municipalities with approximately 1, 375,000 inhabitants. In both plants the sludge came from the primary settling tank and the secondary clarifier, was dewatered (only in Lynetten) by centrifuges before digestion. The digested sludge was dewatered by centrifuges and pre-dried before incineration in the fluidized bed combustor. In both waste water facilities, iron was used to precipitate phosphorus, and the

sewage sludge was incinerated in a fluidized bed combustor at about 850 °C. After sampling, the ashes were stored in closed plastic containers at room temperature.

2.2. Pre-treatment of the ash

Two pre-treatment methods for SSA were used in this study; water washing (W) and grinding (G). Water washing of SSA consisted of 3 washing cycles in distilled water. 100 g of ash was mixed in a 1 L plastic bottle with 500 ml of distilled water and agitated for 1 min. The bottle was then placed in a vertical position until the SSA settled. When settled, water was decanted, and the bottle was refilled with a new dose of 500 ml distilled water. This procedure was repeated 3 times. After the last agitation, water and SSA were decanted through a filter paper (11 µm) and the wet SSA was dried in an oven at 105 °C. In the alternative pre-treatment method, SSA that had not been washed was ground for 30 s in a Vibrating Cup Mill Pulverisette 9. The ash was then dried in an oven at 105 °C.

2.3. Ash characterization

The characterization and extraction experiments were always performed using ash that had been dried at 105 °C for 24 h. An external, commercial laboratory performed XRF analysis. The morphology was studied by means of a Scanning Electron Microscope (SEM) on either ground or water-washed ash. The accelerating voltage of the SEM was 20–25 kV with a large field detector and X-ray cone. Particle size distributions were measured by laser diffraction using a Malvern Mastersizer 2000. A dry dispersion method for moisture sensitive materials was used.

2.4. Preparation of mortar samples

Reference mortar samples based on cement were prepared according to the standard DS/EN 196–1 [13]. For the mortars containing SSA, the same mix design was used, but different proportions of the cement were replaced by SSA. The mortar was cast into prism moulds measuring 4 × 4 × 16 cm. The mortar monoliths were cured for 28 days in a water bath (temperature 20.0 ± 1.0 °C). Two ratios of substitution of cement by SSAs were used: 10% and 30% by weight (see Table 1). The amounts of added water and sand were the same for all mixtures. A basic Aalborg Portland cement was used (Portland limestone cement, strength class 52.5 N) [15]. Sand from Dansand A/S was used and met the requirements defined by the standard with D (0.5) = 0.516 mm (Fig. 2).

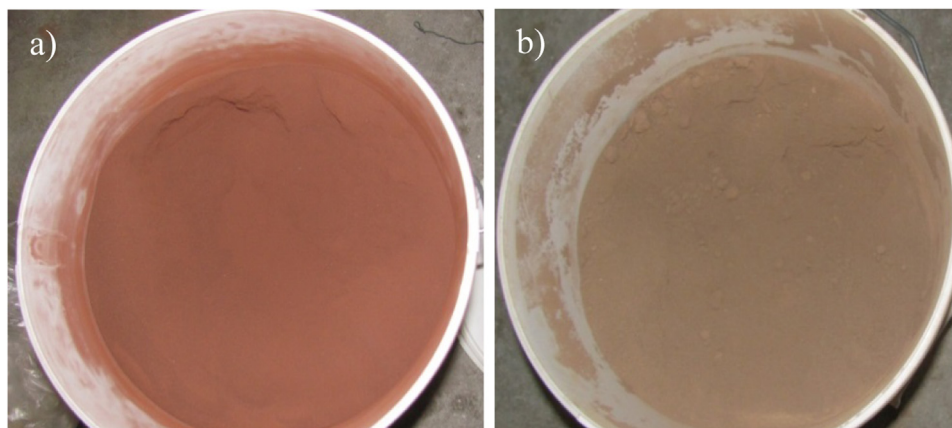


Fig. 1. The two investigated SSAs: a) Avedøre ash (AVE) and b) Lynetten ash (LYN).

Table 1
Basic mortar recipes used in this work (% by weight).

Substitution ration [%]	Cement [g]	SSA [g]	Sand [g]	Water [g]
0 (Ref)	450	0	1350	225
10	405	45	1350	225
30	315	135	1350	225

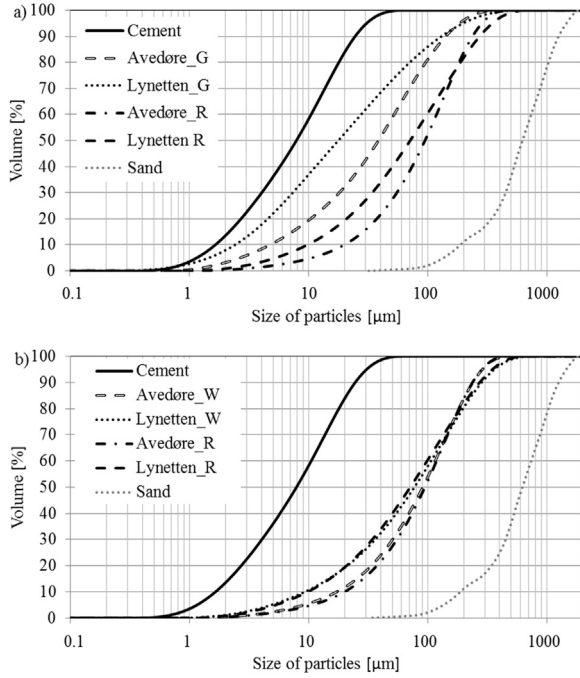


Fig. 2. Particle size distribution – undersize curves; comparisons of Basis cement and SSAs. a) Cement, untreated (R) ash, ash ground (G) for 30 s and sand b) Cement, untreated (R) ash, water-washed (W) ash and sand.

2.5. Water vapour adsorption test of cement, SSAs and mortar samples

A determination of the hygroscopic sorption properties of cement, ashes and mortar samples was performed in accordance with the standard [27]. Moisture storage in the hygroscopic range was determined as moisture content measured at equilibrium for samples exposed to the various levels of relative humidity (RH).

The standard specifies two alternative methods, using either a desiccator or a climatic chamber. In this study a method using glass desiccators was used for determination of the absorption isotherm. The mortar samples were crushed into grains with a maximum size of 5 mm and dried at 45 °C. Reference cement-based samples and samples with 30% cement replacement by SSA were studied. Desiccators, glass weighing cups, a balance and a climatic chamber with constant temperature at 22 °C were used. The relative humidity in each desiccator was maintained with different salt solutions with the following relative humidity: 33%, 58%, 75%, 86% and 94%. The absorption isotherm was derived for 3 replicates of each sample. The mass of the samples was determined using a Sartorius Research R 300S balance. The accuracy of these measurements was ± 0.2 mg.

2.6. Apparent density and open porosity

Measurements of apparent volume V_o and open porosity P_o followed standard DS/EN 772-4 [16] and was performed on 3 replicates. The mass of each sample was determined using a balance with the accuracy of the measurements ± 0.01 g. The apparent density ρ_o considers the solid constituents of the material and the pores in combination. It is defined as the ratio of the dry mass M_{dry} and the volume V_o of the dry

specimen, see Eq. (1).

$$\rho_o = \frac{M_{dry}}{V_o} \tag{1}$$

The open porosity or void ratio is the percentage of open pores in the specimen, see Eq. (2) where V_{pores} is the volume of open pores.

$$P_o = \frac{V_{pores}}{V_o} \tag{2}$$

2.7. Capillary water absorption

The water absorption test followed standard [28] and was performed on 3 replicates of the mortar samples. The samples were partially immersed in water so that only the bottom side was in contact with the water. To ensure one-dimensional transport, the samples were sealed with epoxy on the sides. The weight gain of the samples due to water absorption was determined over time at increasing intervals. The water absorption coefficient A_w is expressed as a mass of water absorbed by a test specimen per surface area and square root of time. The mass of the samples was determined using a Sartorius Research R 300S balance. The accuracy of the measurements was ± 0.2 mg.

2.8. Compressive strength test

The compressive strength of the mortar samples was assessed after 28 days of curing for six replicates of 4 × 4 × 8 cm monolithic prisms (between the ends of the cast specimen). The compressive strength was measured according to the procedure described in the standard DS/EN 196-1 [13]. The work involved nine different mixtures. The substitution ratio of cement varied from 0% (REF) to 10% and 30%. Both types of SSAs were used as substitutes with all substitution ratios and with different pre-treatment methods.

3. Results and discussion

3.1. Chemical characteristics of the SSAs

The presence of certain chemical compounds in cement and ash may affect many aspects of mortar casting, such as hydration degree and its rate, workability, or compressive strength. Even when such compounds are only present in little amounts, they may measurably affect the resultant properties of the binder.

The bulk element oxide concentrations are shown in Table 2. Both ashes contained SiO₂, CaO and Al₂O₃, which are also major constituents

Table 2
Major oxide content and chloride content present in the cement, coal fly ash and SSAs.

Major oxide content [%]	Cement	Coal fly ash*	Avedøre not treated	Lynetten not treated	SSA**
MgO	0.53	0.1–6.7	1.82	1.99	0.02–23.4
Al ₂ O ₃	4.91	2.6–20.5	4.4	2.65	4.4–34.2
SiO ₂	20.1	11.8–46.4	15.83	14.33	14.4–65.0
CaO	65.8	15.1–54.8	23.37	36.38	1.1–40.1
TiO ₂	0.35	0.6–1.0	0.83	0.67	0.3–1.9
Fe ₂ O ₃	5.43	1.4–15.6	16.30	7.15	2.1–30.0
MnO	0.04	0.1–6.7	0.09	0.05	0.03–0.9
K ₂ O	0.81	0.3–9.3	1.45	1.81	0.1–3.1
Na ₂ O	< 0.67	0.2–2.8	0.67	0.81	0.01–6.8
P ₂ O ₅	0.23	0.2–0.4	18.33	10.31	0.3–26.7
SO ₃ ⁻	4.74	1.4–12.9	2.00	4.74	0.01–12.4
Cl ⁻	0.1	–	< 0.01	0.2	–

* Source: Hemalatha and Ramaswamy [24] (coal fly ash Class C).

** Source: Cyr et al. [9] (range of typical min and max values based on literature review).

of ordinary cement. It is known that siliceous or siliceous-aluminous materials, if such compounds are present in amorphous state, react chemically with calcium hydroxide at room temperature, forming compounds that possess cementitious properties. Thus pozzolanic activity is directly related to the chemical composition [39]. According to the European standard [14] “the pozzolanicity is assessed by comparing the concentration of calcium oxide present in the aqueous solution in contact with hydrated cement with the quantity of calcium ion capable of saturating a solution of the same alkalinity. The test provides a positive result if the concentration in the solution is lower than the saturation concentration”. Additionally to their pozzolanicity, the physical characteristics of constituent materials also enhance the strength of cementitious systems, including size, shape and texture of the particles [22]. It is worth noting that the pozzolanic activity depends on the silica crystallization phase, size and surface area of the ash particles [65]. The pozzolanic activity of the two ashes was not explicitly studied but it is assumed that the pozzolanicity of SSAs is low compared to that of cement.

In the ashes, the content of CaO was higher in LYN (36.4%) than in AVE (23.4%), but in LYN the content was slightly above half of the content in cement. Cyr et al. [9] compiled published data on SSA composition and reported that the CaO content in SSAs ranges from 1.1% to 40.1%, so the two SSAs investigated here were within the normal range of other SSAs. The SiO₂ (15.8%) and Al₂O₃ (4.4%) content of AVE was almost that of cement (20.1% and 4.9%, respectively), while LYN contained less SiO₂ (14.3%) and Al₂O₃ (2.7%). The SiO₂ and Al₂O₃ contents of the AVE were within the ranges reported by Cyr et al. [9]: 14.4–65% SiO₂ and 4.4–34.2% Al₂O₃.

It is worth noting that the content of phosphorus pentoxide (P₂O₅) was much higher in the SSAs compared to the cement. A similar range of P₂O₅ concentration in SSA was observed by Cyr et al. [9]: 0.3–26.7%. A high content of P₂O₅ results in longer setting times and slow development of strength [37,43,46]. Regarding the concentration in cement, Hewlett [25] stated that P₂O₅ is occasionally present in small amounts in the raw materials of cement manufacture and in such cases it passes into the clinker. If present in quantities of 1–2% in Portland cement clinker it slows the rate of hardening of the cement [25]. As reported in Table 2, adding SSA to the mortar mixture increased the total content of P₂O₅. This may adversely affect the setting and hardening of the mortar and so may reduce the compressive strength of the material. When 10% of the cement was replaced by AVE ash, the content of P₂O₅ increased by approximately 1.8% compared to cement-based mortar, and with a replacement ratio of 30% the P₂O₅ content increased by 5.2%. In the case of cement replaced by LYN ash with replacement ratios of 10% and 30%, the P₂O₅ content increased by approximately 1%, and 3%, respectively. Such elevated concentrations of P₂O₅ may adversely affect the rate of strength development. However, recent strategies focus on phosphorus removal from SSAs before its use as an SCM.

The content of the 5 oxides with the highest concentrations (Table 2) in the two SSAs were for AVE: CaO > P₂O₅ > Fe₂O₃ > SiO₂ > Al₂O₃ and for LYN: CaO > SiO₂ > P₂O₅ > Fe₂O₃ > SO₃, which reveals, that the two SSAs are of significantly different composition. The higher content of Fe₂O₃ in AVE than LYN corresponds well with the stronger red colour of AVE (Fig. 1), which is due to the presence of iron oxides added during incineration process. In general, the oxide contents of the two studied ashes varied within a typical range of concentration values, or were just in the low end of the range.

The oxide content of SSAs was compared to the coal fly ash described in the study by Hemalatha and Ramaswamy [24] as coal fly ash was used for decades as SCM [4]. The coal fly ash is defined in standard as a fine powder consisting mainly of spherical glassy particles formed during the combustion of pulverized coal. Coal fly ash is obtained by electrostatic or mechanical precipitation of ash particles in the exhaust gases of power plants that combust coal. Similar to cement, coal fly ash contains the reactive oxides SiO₂ and Al₂O₃. The reactive content of SiO₂ according to standard DS/EN 197-1: [15] must be at least 25% of

the ash to be classified as siliceous. However, it is important to note that cement and ash origin are different and this will affect the way the compounds react. Danish coal fly ash, due to its chemical composition and type of combustion, meets the requirements to be classified as siliceous [44]. Nevertheless, there are no corresponding requirements for SSA as an SCM in concrete.

3.2. Particle size distribution of cement and SSA and grain morphology

The particle size distribution and morphology of cement and ash grains have a significant effect on the heat of hydration, the progress of hydration and consequently on mortar porosity and its compressive strength [20,40]. The compressive strength increases with an increasingly narrow particle size distribution (at constant specific surface area), i.e. for equal specific surface areas the strength increases as the grain size distribution becomes narrower. This implies that the heat of hydration and the amount of hydration product both increase when the particle size distribution becomes narrower [34]. The fineness of a particle and the related specific surface area both have a strong effect on the rate at which the cement hydrates when exposed to water [36,7]. If an ash is used as a substitute for cement in mortar production, the smallest particles, with the largest relative surface area, being the most reactive, would act as a binder whereas the biggest particles, being much less reactive, would mainly act as a filler [6].

The grain size distribution for cement, SSAs and sand are seen in Fig. 2. LYN is clearly characterized by finer particles compared to AVE, both in the as-received form (R) and when it had been ground (G). Fig. 2a) shows that after 30 s of grinding, the particle size distribution was shifted and had become closer to that of cement, compared to non-ground samples, as expected. In Fig. 2b), the water-washed (W) ashes follow the curve of untreated ash.

Fig. 3 shows SEM images of the SSAs in both raw and treated forms. The SSA particles were irregular and porous, confirming the previous report by Donatello and Cheeseman [11]. Observations based on SEM images supported with the observed results from the particle size distributions shown above. Grinding, even only for 30 s, improved the fineness of the grains (also reported by Kappel et al. [31]), while the water-washing pre-treatment did not change the morphology.

Sewage sludge ash characteristics obtained by Lynn et al. [38] show that the above grain size distributions correspond to the range of particle size that characterizes silt (2.5–62.5) μm and fine sand (62.5–250) μm. In the present study of the ashes from Lynetten and Avedøre, particle size varied approximately from 1 to 400 μm for untreated ash, while cement particles were in the range (0.4–50) μm. The median particle size of Portland cement was D(0.5) = 8.3 μm, while for the SSAs, D(0.5) = 100 μm was the median particle size for AVE and D(0.5) = 75 μm for LYN. For comparison, sand has a particle size range that extends up to 2000 μm with a median particle size D(0.5) = 520 μm (Fig. 2)).

The particle size range of the ashes was evidently larger than that of Basis Aalborg Portland cement. Additionally, cement had a narrower particle size distribution curve than the SSAs. This may adversely affect the rate of hydration of the mortar mixture. Several studies tested the hydration of cement-based and cement-ash-based pastes [17,26,36,7]. Chen and Poon [7] reported that no heat release was measured when a paste contained only SSA and no cement, indicating that SSA does not possess any hydration activity in itself, and this was confirmed by Cyr et al. [9]. On the other hand, the peak hydration rates of a paste containing both cement and SSA were reported to be higher than those of cement paste [7]. This is probably due to the porous structure of SSA that entraps water in its pores, leading to a higher concentration of cement particles in water, i.e. a lower effective water to cement ratio [26] that exceeds the dilution effect of the cement [35] that was replaced by SSA. The effect of the grain size distribution and morphology of the two specific SSAs after different pre-treatments on the hydration progress of mortar was not part of the study but would be a suitable

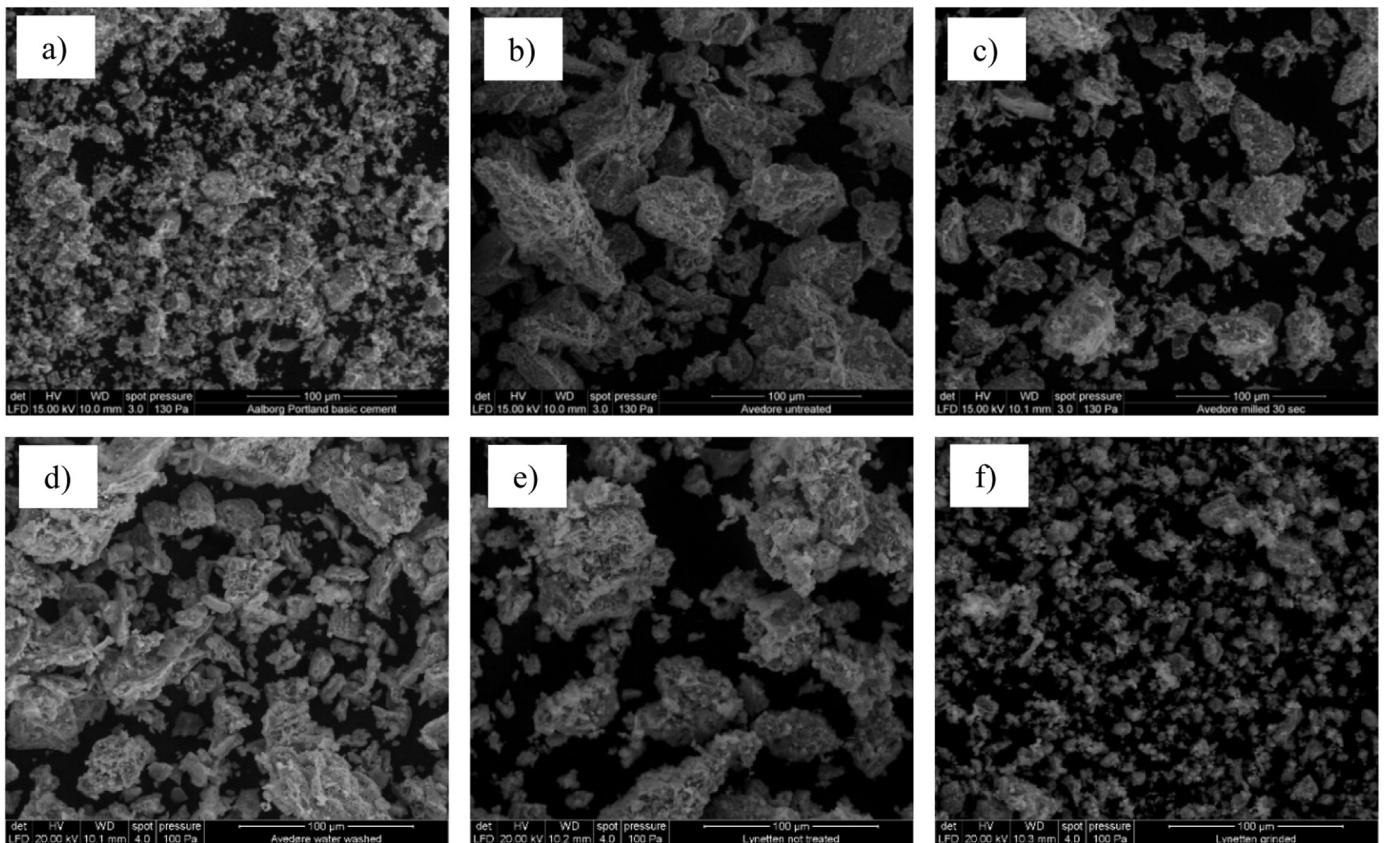


Fig. 3. Scanning electron microscope images a) cement, b) AVE not treated, c) AVE grinded for 30 s, d) AVE water washed, and e) LYN not treated, f) LYN grinded for 30 s.

subject for further investigations.

3.3. Water vapour adsorption test of the cement, SSAs and mortar samples

The water vapour adsorption capability of cement and of ground and water-washed SSAs are shown in Fig. 4. Adsorption data for mortar samples are presented for comparison in Fig. 4, and these results will be further discussed in a later report of the study. The graph clearly reveals that the moisture adsorption of cement is higher than that of the SSAs when exposed to identical conditions. The effect of relative humidity on cement hydration has been studied by some authors, although most of them studied cement pastes [50,52,62]. They reported that hydration virtually ceased below about 80% RH. These results indicate that the amount of water in the capillary structure of the paste is important for

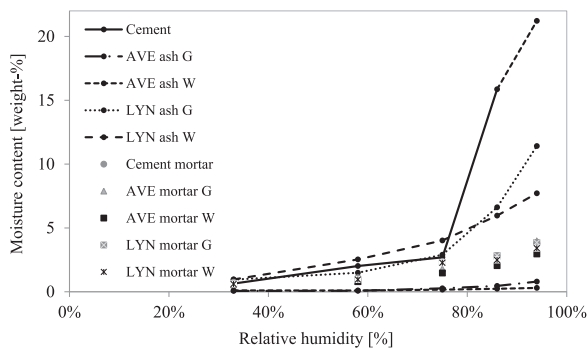


Fig. 4. Sorption isotherms of the cement, treated SSAs, cement mortar and mortar with 30% treated SSA as SCM. (AVE – Avedøre ash, LYN – Lynetten ash, G – ground, W – water-washed). The sorption curve of cement did not reach equilibrium above 86% RH and the line is thus dashed.

hydration to proceed [50]. The cement data in Fig. 4 show that the steepest increase of the adsorption curve was observed above 70% RH, which lends support to the previous experimental observations. The last step in the sorption curve of cement (dashed line from 86% to 94%) demonstrates a step that did not reach equilibrium for the conditions at 94% RH, while the ashes did so. This may be due to the reactions of the cement clinker components with water as cement requires a long period of time to become fully hydrated [45]. When water is present as vapour, the cement reactions are slower than when water is present in the liquid phase, so cement continued to react with water vapour, while the SSAs had already reached equilibrium. These observations are in agreement with the statement by Chen and Poon [7] that SSA does not hydrate itself, it just entraps water in its pores.

By comparing the adsorption curves of the SSAs it can be seen that each SSA has a different sorption capacity. It is evident that LYN ash adsorbed more moisture at all values of RH, both in the ground and water-washed form, compared to AVE. For example, AVE adsorbed less than 1 wt% at 94% RH, whereas at the same RH, water-washed LYN adsorbed more than 7% water by weight, and ground LYN ash adsorbed even more water vapour. This is linked to the finer particle sizes of LYN ash (Fig. 2), which gives it a larger relative surface area. Comparing the different pre-treatment methods, the ground SSAs had higher water vapour sorption capacity at the highest RH than the water-washed samples. Although grinding increased the relative surface area of grains [48,7], this might also be due to the presence of water-soluble hygroscopic salts in ground ash, while these were washed out or were incorporated into new particles in the water-washed SSAs.

In addition to the adsorption isotherms for the treated SSAs, Fig. 4 also shows the sorption values of hardened mortars: cement mortar and mortars containing the SSAs (30% as an SCM). The sorption results of different mortar compositions almost overlap each other over the major part of the relative humidity range in the common scale perspective for

ashes and mortar. Minimal or no differences in mortar adsorption were found between the different ash pre-treatments. Based on a comparison of sorption curves for cement and SSA particles, where differences between the individual components are clearly visible, the measurements of the mortars were not, or only to a minimal extent affected by replacement of up to 30% of the cement content. However, there was a tendency for the mortar with washed SSA to be slightly lower in water vapour sorption than mortar containing ground ash.

3.4. Open porosity and apparent density of mortar

The porosity of a material normally has a considerable influence on its physical properties. Mortar is a porous solid, which by its nature has properties based on its constituents and their chemical reactivity. When a concentrated suspension of cement and ash in water is allowed to hydrate, the reaction products are formed as a coherent matrix that encloses the residues of non-hydrated grains. The hydration process may take place over a long period, even after the set hardening period, and the matrix retains some of its porosity while hydration continues [34]. This implies that the density and porosity of the material reflects the hydration state of the mortar. A simple empirical relationship between strength and porosity has been found in data for hardened cement pastes [53]. A reduction of porosity in a solid material increases its strength in general, and the strength of cement-based materials in particular [18,63]. The compressive strength and its relation to porosity will be discussed further in the following section. It is to be expected that SSA would have a considerable effect on mortar porosity, as SSA itself is a porous material. However, for the benefit of mortar compactness, the pores in an SSA might serve as a place to accommodate hydration products [66].

The apparent density and open porosity of the different mortars (Fig. 5) indicate a minor influence of ash content on apparent density, while its influence on porosity was more obvious. The density slightly decreased (and the porosity increased) as the content of SSA increased, which may be because the SSA had a lower density than the cement or because of the irregular morphology of ash grains [2]. It is clear that the increase of porosity was linked to the decrease of density, as these two parameters are directly related. The lowest porosity was observed for the REF mortar where only cement was present. Such a phenomenon is based on the fact that cement is reactive with water and thus has lower porosity at equal density. In general, a small effect of ash content on porosity was observed with 10% cement replacement by SSA (AVE10G, LYN10G) compared to REF. As Chen and Poon [7] reported, substitution of up to 10% of cement by SSA balances the effect of higher porosity with improved hydration of cement, using the water absorbed in the ash pores. An increase in porosity by more than 20% was found for AVE30W compared to REF. It has been shown in the previous section that simple grinding for 30 s provided finer ash grains. This resulted in no significant changes in the porous structure of the material when only 10% of the cement was replaced, for example for AVE10G vs. AVE10W,

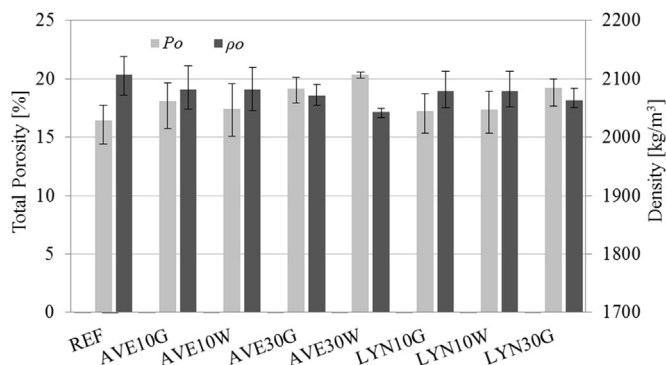


Fig. 5. Apparent density ρ_o and open porosity P_o including standard deviation.

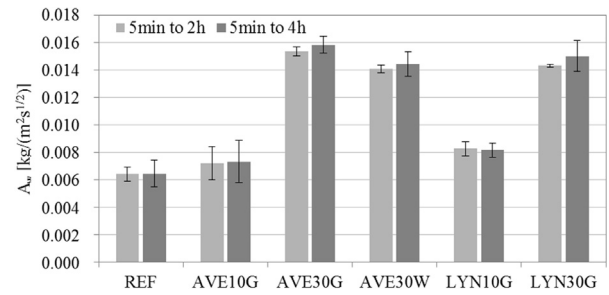


Fig. 6. Water absorption coefficients for mortars with different grades of SCM and their standard deviations. A_w was determined for two different time intervals.

and LYN10G vs. LYN10W. The effect of ash grinding was slightly visible at a replacement ratio of 30%, i.e. when comparing AVE30G with AVE30W. These observations imply that mortar porosity increased with increased ash to cement ratio. Additionally, the porosity of the mortar with ground SSAs slightly decreased as the fineness of the SSA increased.

3.5. Capillary absorption (Water uptake)

The results of the capillary water absorption tests are shown in Fig. 6 as water absorption coefficients. Only the linear transient part of the measured curve was considered. As proof of the accuracy of the measured data, results from two time-periods are presented: one period considered immersion time intervals between 5 min and 2 h, while the second considered intervals between 5 min and 4 h. As may be seen, the water absorption coefficient increased significantly with the ash to cement ratio, but it was not affected either by ash type or ash pre-treatment method. Mortars containing 30% SSA had water-absorption coefficients of about 2.5 times the value for REF cement mortar. This indicates that the higher porosity of the mortars that contain SSA have more pores in the capillary range than the purely cement-based mortar. The fineness of the SSA has no significant influence on the capillary water absorption of the cast mortar. However, the water absorption coefficient is slightly higher for AVE30G compared to AVE30W. This slight difference may be due to an increased number of capillary pores in AVE30G, as the grinding pre-treatment leads to a finer particle size and higher surface area [26,48].

3.6. Compressive strength

Compressive strength is one of the most important characteristics of a structural building material. This parameter was therefore included in the test schedule despite the large amount of published data on the subject. A test of compressive strength was performed in order to investigate the practical applicability of mortar with a high cement replacement ratio by SSA. It is well known that compressive strength may be affected by the presence of both major and minor components in clinker and ash, the specific surface area of grains, the particle size distribution and the microstructure of grains [34]. Some of these aspects were already discussed above.

It was observed that the mixtures in the fresh state containing ash had less workability when compared to the mixture with no ash, although the consistency was still sufficiently liquid for casting to be possible without adding extra water. This may be caused by the irregular shape (unlike coal fly ash with its spherical grain shape) of the ash particles, by the porous structure of the SSAs' particles [10] and high content of P_2O_5 [34,46] adversely affecting workability, setting time and strength development. This implies that either some of the water added during casting may be absorbed by the irregular particles of ash, or that P_2O_5 forms a matrix, while consuming the water, with the reactive CaO and SiO_2 reducing their availability for pozzolanic reactions

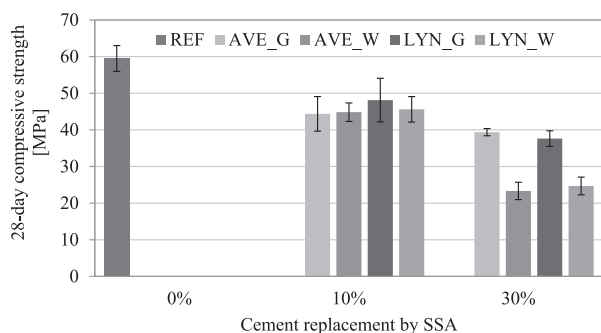


Fig. 7. 28-day compressive strengths of mortar test specimens.

and resulting in longer setting time and delays of hydration [51] and subsequently in strength drop [46]. As a consequence of irregular shape of particles, less water is available to provide proper workability than for the reference cement-based mortar. Whether this water is still available for the hydration process or is permanently captured by the particles has not been investigated.

Fig. 7 shows the compressive strength of the mortar samples of this investigation after 28 days of curing. The compressive strength, in general, decreased with increasing ash content compared to the reference mortar. It has previously been studied that grinding of SSA may improve the ash quality with respect to its use as an SCM [12,30,47,49]. The results obtained in this study support the previous findings [47], in which increased compressive strength was reported for samples containing SSA that had been ground for 30 s compared to SSA treated by water washing. A more evident effect was observed for 30% cement replacement by SSA, in terms of compressive strength loss.

The mortar strength is primarily dependent on the binder, the water to cement ratio, its porosity and its density. Higher material porosity would result in a lower final strength of the material. In the present study, replacement of 30% cement content by the pre-treated SSA resulted in an increase in porosity of more than 20% and a decrease in compressive strength of more than 50% at 28 days (AVE30W). The mortar with the lowest cement to ash ratio possessed the highest porosity and thus the lowest compressive strength, as expected. The water to binder ratio was kept constant, but the water to cement ratio increased from 0.5 to 0.7, which must also be expected to influence the compressive strength (as well as the porosity), as the SSA does not directly substitute for the hydration reactions of the cement. Several studies tested the compressive strength of mortar with various cement substitution ratios (up to 20%) at different ages, i.e. 7-day, 28-day and 90-day [29,43,7,9]. As in the observations described above, it was unanimously reported that, with increased substitution ratio of cement by SSA, compressive strength decreased. However, it was also reported in the foregoing publications that the compressive strength continuously developed over time for all the samples (both cement-based and cement-ash-based) at all time periods. There are some possible explanations of strength development of cement-ash-based mortar over time: firstly the water absorbed by the ash pores reduces the water to binder ratio, which counterbalances the dilution effect (i.e. higher water to cement ratio), secondly the water absorbed by the ash pores may be released back to the matrix allowing additional hydration of cement. Additionally, the irregular shape of ash particles enhances the interlocking among grains of ash and cement and supporting overall strength.

4. Conclusions

Two sewage sludge ashes (SSA) with two different pre-treatments, namely water washing and grinding, were studied in this investigation to ascertain the consequences of using them as supplementary cementitious material (SCM) with replacement levels of 10% and 30% of

the cement in mortar. Both ashes contained silicon dioxide (SiO_2), aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3) similarly to cement, so some cementitious properties may be anticipated. However, no XRD analysis was carried out to ascertain degree of crystallinity and to establish pozzolanicity. In addition, a high content of phosphorus pentoxide (P_2O_5) was detected, which may adversely affect the mortar setting and hardening process.

Sorption isotherms showed that the hygroscopic water vapour absorption of the two types of SSA was different. For one of the ashes, the adsorption was less than 1% by mass at 94% RH, regardless of the pre-treatment method, while the other absorbed more than 7% at the same RH (the ground ash more than the water washed ash). The difference is believed to be due to differences in the fineness of the particles and in the content of hygroscopic salts. However, the effect of the SCMs on the water vapour sorption of the cast mortars was minor, even with 30% cement substitution. It was concluded that the final mortars are not significantly affected by the sorption properties of cement and SSAs.

Particle size distributions indicated larger grain sizes of SSA compared to cement. Finer particle sizes were achieved by grinding the ash as a pre-treatment. Finer particle sizes were achieved by grinding the ash as a pre-treatment. Pre-treatment by water washing did not influence the particle size distribution. The porosity of mortar was clearly affected by the particle size of each constituent. The mortars with the highest ratio of SSA were the most porous. Generally, the porosity was slightly influenced by the pre-treatment method at the highest ratio of cement substitution. Similarly, the capillary water absorption coefficient increased in mortars with SSA compared to the reference cement-based mortar and with increasing SSA content. The particle size distribution clearly affected the compressive strength, and even 10% cement substitution by SSA caused a significant decrease in the 28-day compressive strength of mortar. At cement to ash ratio of (7:3), clear differences between ash pre-treatment methods were observed: grinding the ash resulted in improved compressive strength compared to the water-washing pre-treatment.

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Declaration of conflicting interests

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Paper II

Barbora Krejcirikova, Carsten Rode and Ruut Peuhkuri (2018) Determination of hygrothermal parameter of cementitious mortar: The effect of partial replacement of cement by incinerated sewage sludge ash, *Journal of Building Physics*, 42(2), 771-787.

Determination of hygrothermal properties of cementitious mortar: The effect of partial replacement of cement by incinerated sewage sludge ash

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and Ruut Peuhkuri²

Abstract

Two sewage sludge ashes were used as substitutes for cement and their effect on the hygrothermal properties of mortar was examined. Different cement to ash ratios and two ash pre-treatment methods (water washing and grinding) were in focus. The impact of cement replacement by sewage sludge ashes on thermal conductivity, sorption isotherms, water vapour permeability and carbonation was described with standard cement-based mortar as the reference material. Measurement results showed that thermal conductivity decreased by 15% when 30% of the cement was replaced by sewage sludge ash. Water vapour permeability increased as the cement to ash ratio was reduced. Sorption was tested by two methods; although differences in the sorption isotherms of mortars were reported when a climatic chamber method was applied, no differences, or only minor differences, were observed with the desiccator method. Measurements revealed that cement-based mortar possessed a higher content of carbonate than cement-ash-based mortar, and it thus appears that the carbonation rate was higher when the cement content was high.

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Keywords

Sewage sludge ash, supplementary cementitious material (SCM), thermal conductivity, sorption, water vapour permeability, carbonation

Introduction

Sewage is the collection of discharge from domestic, medical, commercial and industrial establishments with added rain water. Sewage sludge has been used in agriculture as a fertilizer due to its high content of phosphorus. More recently, the tendency has been to incinerate sewage sludge (Naamane et al., 2016). The organic matter is combusted and by-products such as CO₂, other trace gases and water vapour are produced. However, the process of waste disposal by incineration is not complete since a non-negligible amount of residue of incinerated sewage sludge ash (SSA) remains afterwards. It is estimated that the global production of SSA is approximately 1.7 million tons annually, mainly from the United States, the European Union (EU) and Japan, and this quantity is increasing (Cyr et al., 2007; Murakami et al., 2009). Most of the SSAs have been landfilled (Ahmaruzzaman, 2010; Chen et al., 2013; Donatello and Cheeseman, 2013; Ottosen et al., 2016), although there has been some exploration of recycling and beneficial resource recovery (Chen et al., 2013; Cyr et al., 2007; Donatello, 2009; Donatello and Cheeseman, 2013; Halliday et al., 2012; Ing et al., 2016; Lynn et al., 2015; Monzó et al., 1996, 2003; Pérez-Carrión et al., 2014; Smol et al., 2015; Wiebusch and Seyfried, 1997; Yusuf et al., 2012). These investigations included the potential use of SSA as a supplementary material in blended cements (Cyr et al., 2007; Garcés et al., 2008), mortar (Lin et al., 2008; Monzó et al., 2003; Yusuf et al., 2012), blocks (Baeza-Brotons et al., 2014; Pérez-Carrión et al., 2014) and bricks (Eliche-Quesada et al., 2011; Weng et al., 2003). The role of the SSA in mortar can be either as a cement substitute (similar to coal fly ash), thus as a binder when it possesses some degree of pozzolanic activity, or it may replace sand and thus act as a filler. Such replacement would not only preserve natural resources but also significantly contribute to a reduction in CO₂ emissions and to increased energy conservation in the course of cement production and waste handling (Benhelal et al., 2013; Hasanbeigi et al., 2012; Worrell et al., 2001). These benefits will be substantial, as the cement industry produces 3.4 billion tons of cement annually, which contributes to 5% of all CO₂ emissions caused by human activity (Benhelal et al., 2013) and accounts for 2% of global energy consumption (Worrell et al., 2001).

This study was performed in the 'ZeroWaste' development area at the Department of Civil Engineering of the Technical University of Denmark (DTU) (ZeroWaste Byg, 2017), which was intended to develop new construction materials based on partial replacement of ordinary material constituents with secondary resources such as recycled materials. Characterization of two ashes and their effect on selected physical properties of mortar were described in a previous part of the study (Krejcirikova et al., in press). The aim of this work is to comprehensively

assess the effect of cement replacement by two specific SSAs at different replacement ratios and with two ash pre-treatment methods on the heat and moisture transport properties of mortar.

Materials and methods

Material samples

Mortar mixture. SSAs from two different locations were used in this study as a partial replacement material for cement. One type of SSA originated from a wastewater treatment plant in ‘Avedøre’ (AVE), while the other was from ‘Lynetten’ (LYN). Both of these plants are located near Copenhagen, Denmark. The plants treat wastewater from 17 municipalities that together serve approximately 1,375,000 inhabitants.

As a reference material (REF), cement-based mortar samples (being mixtures of water, cement and sand) were prepared according to the standard DS/EN 196-1:2005, with the water–cement ratio kept constant at 1:2 for all mixtures. The same recipe was used for cement-ash-based mortars in which the cement content was partly replaced by specific ashes, with mixtures and substitutions as shown in Table 1. After casting and curing for 24 h in a moist atmosphere, the samples were demoulded and the mortar monoliths were cured for 28 days in water at a constant temperature of $20 \pm 1^\circ\text{C}$. The samples were then stored and dried in an oven at 45°C .

Pre-treatment of ashes. Two different pre-treatment methods were applied to the ashes: grinding or water washing. As reported in Krejcirikova et al. (in press) and Ottosen et al. (2013), a simple ash pre-treatment can improve the compressive strength of the mortar.

Table 1. A matrix of mortar mixtures used in the study.

Name	Substitution ration (%)	Ash origin	Pre-treatment
REF	0	X	X
AVE 10G	10	AVE	G
AVE 10W	10	AVE	W
LYN 10G	10	LYN	G
LYN 10W	10	LYN	W
AVE 30G	30	AVE	G
AVE 30W	30	AVE	W
LYN 30G	30	LYN	G

The designations of the samples derive from their origin (Avedøre, AVE, or Lynetten, LYN), their substitution ratio (10 or 30) and the pre-treatment applied (grinding, G, or water washing, W).

Water washing of the SSA consisted of three washing cycles in distilled water. In a 1-L plastic bottle, 100 g of ash was mixed with 500 mL of distilled water and agitated for 1 min. Afterwards, the bottle was placed in a vertical position until the SSA settled. When settled, water was decanted and the bottle was refilled with a new dose of distilled water. This procedure was repeated three times. During the last cycle, water and SSA were decanted through a filter paper (11 μm). The wet ash was then dried in an oven at 105°C for at least 24 h, and after cooling it was ready for use.

The other pre-treatment method was ash grinding. In this case, ash was ground for 30 s to achieve a finer particle size, using a Vibrating Cup Mill Pulverisette 9. After grinding, the ash was dried in the oven at 105°C, and after cooling it was used in the mortar production.

Experimental methods

Drying. The samples were dried either in an electrical oven or in a desiccator with silica gel. The samples used for sorption tests in the climatic chambers were exposed to different environments in order to determine their dry mass under various conditions. Prior to the sorption experiment, the samples were dried in an oven at 45°C. Approximately 1.5 years after the sorption experiment, the samples were again dried, but now in various environments:

In a sealed desiccator with silica gel at 20°C;

In a ventilated oven with silica gel inside at 45°C;

In a ventilated oven at 105°C;

In a ventilated climatic chamber with a silica gel bag inside at 20°C (in contrast to the desiccator method, CO₂ access was not limited).

Samples were not exposed initially to more than 45°C, to avoid possible structural changes due to their exposure to elevated temperatures and to ensure that the material was exposed to conditions relevant for typical central-European indoor climates. Mass changes were captured by regular weighing using a Sartorius Research R 300 S microbalance with an accuracy of ± 0.02 mg.

Thermal conductivity and volumetric heat capacity. The thermal conductivity and volumetric heat capacity were determined under laboratory conditions at an average temperature of 24°C using a heat transfer analyser, ISOMET 2104. Measurements were performed with a surface probe with a disc sensor. The specific heat capacity c_p (J/(kg K)) was calculated by dividing the measured volumetric heat capacity C_p (J/(m³ K)) by the measured density ρ (kg/m³). Dry and conditioned samples of dimensions 30 cm \times 30 cm \times 3 cm were examined at five surface points. The measuring accuracy was according to the producer: 10% of the reading for thermal conductivity in the range 0.7–6.0 W/(m K) and 15% of the reading for volumetric heat capacity – around 1×10^3 J/(m³ K).

Sorption and moisture fixation. The hygroscopic sorption properties were measured in accordance with the standard ISO 12571:2000. Moisture storage in the hygroscopic range was determined by exposing the samples to various levels of relative humidity (RH). Once equilibrium had been reached, moisture content was determined by weighing. The standard specifies two alternative methods that can be used, that is, the desiccator method and the climatic chamber method. In this study, both methods were applied and were compared. For both of the sorption tests, samples were crushed into pieces of a few millimetres (up to 5 mm) in maximum size and placed in glass cups (three cups per sample) or in inert textile bags (three bags per sample). All samples were dried in an oven at 45°C prior to the experiment (RH in the oven was approximately 10%). RH levels set in the climatic chamber were the following: 11%, 30%, 50%, 70%, 85%, 93% and 96%, and in the desiccators it was as follows: 33%, 58%, 75%, 86% and 94%. In the climatic chamber, only the adsorption isotherm was determined, so the RH level increased once equilibrium had been reached. In contrast, the samples in the glass desiccators were exposed to a high level of RH (100%) first, and RH levels were then progressively reduced in order to determine the desorption isotherms. The samples from the desiccators were then dried in an oven (45°C) and subjected to moisture uptake in an adsorption process.

Water vapour permeability. The water vapour permeability was determined experimentally using the cup method to create an RH gradient in such a way that a steady one-dimensional transport across the samples was attained, as described in the standard ISO 12572:2001. In dry cup tests, silica gel was used as a desiccant to achieve low RH close to 0%, while potassium nitrate (KNO₃) was used to generate a high RH of 93% ± 0.66% in the wet cups. All the assemblies were placed in a temperature- and humidity-controlled chamber and exposed to constant conditions of temperature 23 ± 1°C and RH 53% ± 3%. By regular weighing, the rate of water vapour transmission was determined. Based on the results determined from the first measurements (on 3-month-old samples), the dry cup test was repeated a year after the first dry cup tests. The material parameters were expressed in terms of the water vapour permeance W (kg/(s Pa)) (Equation 1) and water vapour permeability δ (kg/(m s Pa)) (Equation 2). The resistance of the air layer was not considered since the air layer resistance is negligible compared to the resistance of the mortar ($W = \times 10^{-12}$ kg/(s Pa) (air) and $\times 10^{-10}$ kg/(s Pa) (mortar), $\delta = \times 10^{-10}$ kg/(m s Pa) (air) and $\times 10^{-12}$ kg/(m s Pa) (mortar), respectively)

$$W = \frac{G}{A \cdot \Delta p_v} \quad (1)$$

$$\delta = W \cdot d \quad (2)$$

where G (kg/s) is the moisture mass change rate, A (m²) is the transmission area, Δp_v (Pa) is the vapour pressure difference over the sample and d (m) is the thickness of the sample.

Carbonation test. Dry mortar samples were ground into ‘flour-like’ powder and immersed in a hydrochloric acid (HCl) solution. Calcium carbonate CaCO_3 , a product of carbonation, reacted with hydrochloric acid to form calcium chloride (CaCl_2), carbon dioxide (CO_2) and water. The concentration of CO_2 was measured and based on that the content of CaCO_3 was calculated (Table 2).

Table 2. Characterization of samples used in the carbonation test.

Name	Description
New I	Freshly cast samples, cured for 28 days in water, then dried and tested
New II	The same batch as New I but 1 month older, dried in an oven at 45°C
New III	The same batch as New I, dried in an oven at 45°C, exposed to 50% RH for 8 weeks before carbonation test took place

RH: relative humidity.

Results

Drying methods

The dry mass of the mortar specimens presented in Table 3 shows that the most effective drying took place at the beginning of the experiment, immediately after the samples had been taken out of the water curing bath. None of the other methods achieved a lower dry mass compared to the initial drying.

Table 3. Average weight difference (%) of three mortar specimens based on different drying methods compared to the initial drying in the oven at 45°C.^a

Material	Oven 45°C ^a	Desiccator + silica gel		Oven 45°C + silica gel		Oven 105°C		Climatic chamber + silica gel 4% RH	
	(g)	(%)	SD (%)	(%)	SD (%)	(%)	SD (%)	(%)	SD (%)
REF	17.5	4.6	0.29	4.2	0.01	3.0	0.25	3.2	0.32
AVE 30G	19.1	3.0	0.28	3.1	0.23	2.3	0.34	2.1	0.19
AVE 30W	21.2	3.0	0.05	3.2	0.05	2.5	0.09	2.4	0.18
LYN 30G	19.3	3.0	0.18	3.2	0.16	2.2	0.14	1.8	0.25

SD: standard deviation; REF: reference material; AVE: Avedøre; LYN: Lynetten.

^aWeight of mortar samples immediately after initial drying in an oven at 45°C (drying performed immediately after 28-day curing in a water bath).

Comparing the amount of moisture released in the given condition, cement-based mortar (REF) had the lowest ability to release the moisture compared to the mortar samples containing 70% cement and 30% SSA. The ability to release the moisture content increased with the ash to cement ratio. No effect of ash type or ash pre-treatment was observed.

Thermal conductivity and specific heat capacity

Figure 1 shows the relation between the porosity of the mortar and its thermal conductivity. Mortar porosity was clearly influenced by ash content. A coarser ash texture than the fine cement resulted in a higher porosity in the mortar containing ash compared to the REF. The grain size distributions of cement and ashes, their chemical composition and their ability to hydrate, all have significant effects on mortar porosity. These findings were reported in Krejčířikova et al. (in press).

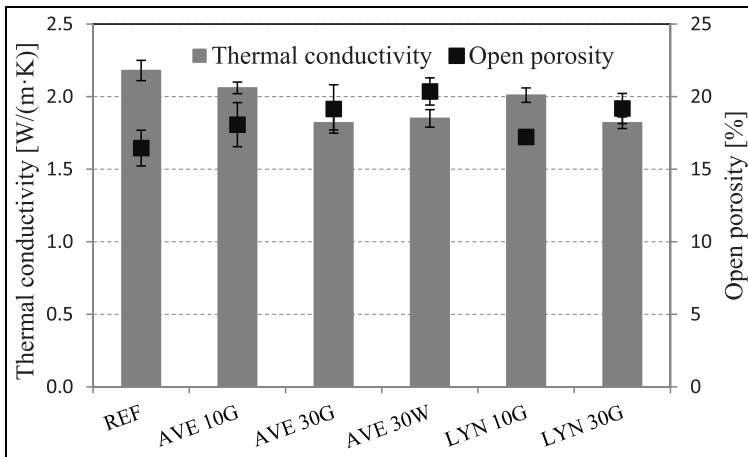


Figure 1. Average values and standard deviations of three duplicates for thermal conductivity and porosity, graphical relation.

The thermal conductivity and specific heat capacity results are shown in Table 4. As expected, thermal conductivity increased with decreasing porosity as the insulating ability of air is greater than that of the solid constituents of mortar. Specifically, the reference material with 0% ash has the highest ability to conduct heat

Table 4. Average values of three duplicates for thermal conductivity λ and specific heat capacity c_p measured by the surface probe of a heat transfer analyser.

Material	λ (W/m K)	SD	Diff. (%)	c_p (J/kg K)
REF	2.18	0.07	—	821
AVE 10G	2.06	0.04	−5.5	822
AVE 30G	1.82	0.05	−16.5	806
AVE 30W	1.85	0.06	−15.1	808
LYN 10G	2.01	0.05	−7.8	813
LYN 30G	.82	0.04	−16.5	814

SD: standard deviation; REF: reference material; AVE: Avedøre; LYN: Lynetten

compared to the mortar containing ash. Replacement of 30% of the cement by ash led to an approximately 15% decrease in the thermal conductivity, which may be an additional advantage for cement substitution. No significant differences in terms of these measurements were observed between the two ashes or between their pre-treatment methods.

Sorption and analyses of moisture fixation

Equilibrium moisture content for specific mortar compositions was measured by two experimental setups: in a climatic chamber and in glass desiccators. Results obtained in tests are presented in this subsection.

In Figure 2, exposure to low RH in the adsorption test in the climatic chamber, that is, at 11% RH, shows that the moisture content of the mortar remained unchanged or even slightly decreased in all the samples compared to its state after initial drying in an oven at 45°C. This indicates that the moisture content in the samples initially after drying was higher than or equal to the equilibrium moisture content at the first RH value imposed in the climatic chamber during the sorption test, that is, at 11% RH. The reference material, REF, without ash content is clearly characterized by having the highest moisture content at all RH levels compared to the specimens containing 10% or 30% of ash. This difference became more pronounced with increasing RH level. In general, for increasing ash to cement ratio, the moisture content became lower. No clear effects of the type of ash or the ash pre-treatment were found.

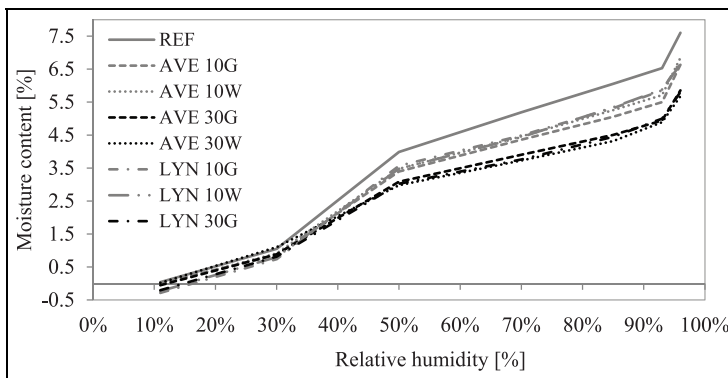


Figure 2. Sorption isotherms of the mortar samples performed in the climatic chamber based on average values of three duplicates.

Figure 3 shows the adsorption and desorption isotherms of hardened mortars, comparing REF mortar with mortar containing AVE or LYN ash as a partial

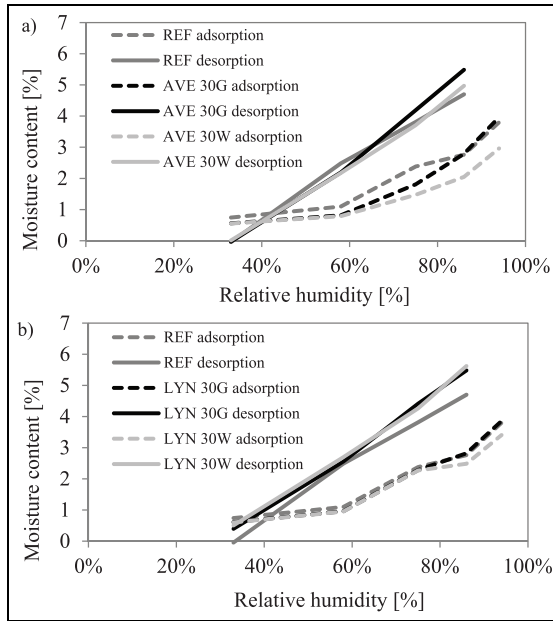


Figure 3. Sorption hysteresis of the mortar samples performed in the desiccators: (a) comparison of cement-based mortar (REF) and mortar with 30% cement replacement by Avedøre (AVE) ash and (b) comparison of cement-based mortar (REF) and mortar with 30% cement replacement by Lynetten (LYN) ash.

cement replacement. Comparing the different mortar compositions, the graphs show that the sorption or desorption curves coincide with each other over the greater part of the RH, although some differences can be observed at high humidity. Only small differences or no difference at all were found between the different ash pre-treatments. However, a slightly higher sorption ability is evident for mortar with AVE 30G, which reached the level of cement-based mortar at RH levels above 80%.

Water vapour permeability

Measurements of the water vapour permeability are shown in Figure 4. Comparing the different mortar compositions, the water vapour permeability increased with the ash to cement ratio. Comparing pre-treatment methods, the results show that using ground ash with a finer ash structure kept the open porosity lower, so the permeability remained lower.

An analysis of results from the dry cup tests and its repetition 1 year later showed a significant decrease in the water vapour permeability with the age of the cementitious material. This may be due to the microstructural evolution of the

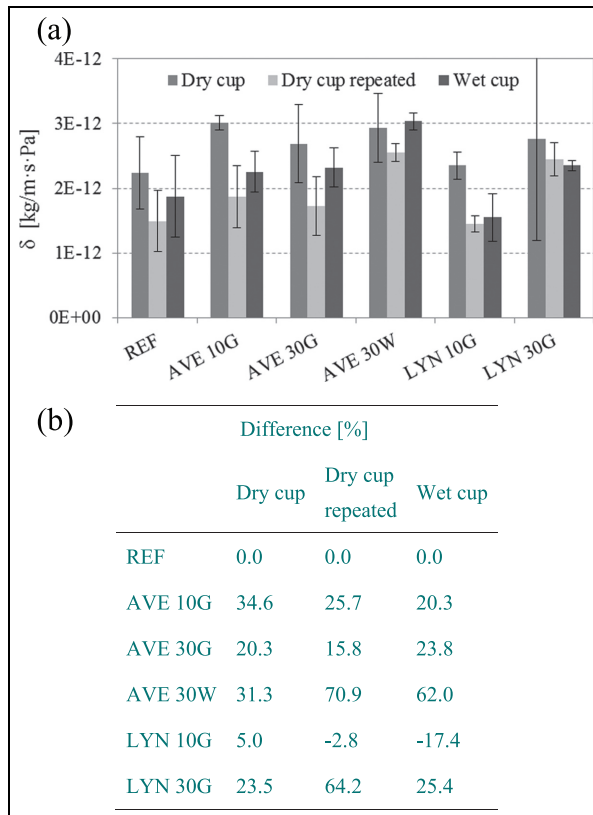


Figure 4. (a) Average values of three duplicates for water vapour permeability δ ($\text{kg}/(\text{m s Pa})$) of the mortar samples and standard deviation (SD), and (b) percentage difference of samples containing ash compared to cement-based mortar (REF).

cementitious material (e.g. porosity and tortuosity) resulting from the processes of hydration and carbonation.

Carbonation test

Figure 5 shows the calcium carbonate content in newly cast mortars that were prepared for the purpose of carbonation test and had never been used in other tests. The observations show that the initial calcium carbonate content in ‘New I’ varied between 12.2% and 13.1%, and thus, its level was similar for all mortar samples regardless of their ash content.

The content of calcium oxide (CaO) naturally occurring in cement and in the SSAs may potentially form CaCO_3 in reaction with CO_2 (Equation 3), resulting in

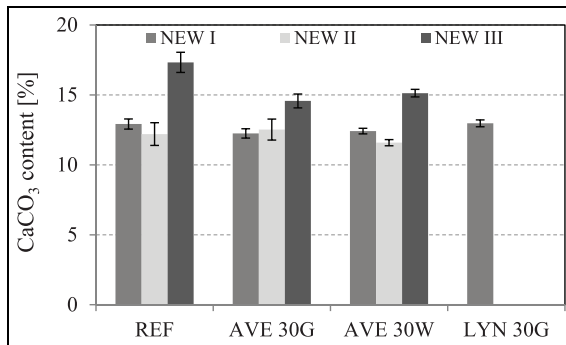


Figure 5. Results of the carbonation test shown as CaCO₃ content in mortar samples.

similar amounts of calcium carbonate (CaCO₃) content in mortar with and without ash (Krejcirikova et al., in press). Comparison of ‘New I’ and ‘New II’ shows that drying in the oven slightly affected carbonate content. While exposure to 50% RH for 8 weeks had a significant impact on mortar carbonation, the calcium carbonate content increased by 2.1%–2.5% steps in samples containing 30% of AVE ash and by 5.1% steps in cement-based mortar samples (REF). Separate carbonation tests indicate that this reaction takes place quite fast



(reversible at high temperature above 825°C) (Powers, 1948)

Discussion

The dry weight of samples is a central parameter for the determination of hygro-thermal properties. Without knowledge of the dry mass, it is impossible to define many parameters such as porosity, density, moisture content, water vapour permeability and water retention. However, in the case of cementitious materials, the dry state is not clearly defined. Cementitious materials naturally contain water that is either bonded in the structure in the form of a C-S-H gel and portlandite Ca(OH)₂ or which is physically present in the pores (Pihlajavaara, 1963), so depending on the drying method, different amounts of water can be expelled. Some studies, for example, Abdelhamid et al. (2016) and Pham (2014a), refer to the drying temperature set to 105°C. Such an elevated temperature may, however, cause structural change to the material. For the purpose of this study with its focus on the interaction of mortar with indoor climate, the drying temperature was initially set to 45°C. Based on the observations, the most effective drying was achieved at the beginning of the experimental testing, just after the samples had been cured. Furthermore, the higher the temperature applied, the better drying results were observed.

Determination of basic material parameters, such as porosity, is an integral part of the material characterization and should not be omitted when reporting on the hygrothermal performance. This study reports only on open porosity in relation to the thermal conductivity of mortar samples. More detailed results can be found in Krejcirikova et al. (in press). The open porosity affects the following hygrothermal properties most: (a) the thermal conductivity, which decreases as the open porosity increases. Pores filled with air serve as thermal insulation and thus decrease the overall thermal conductivity of the mortar. In addition, the thermal conductivity of SSA has been observed to be lower than that of pure cement paste (Wang et al., 2005). (b) Similar observations were made for the water vapour permeability, which was clearly higher for mortars with high ash content. Moreover, it may be concluded that grinding the ash before casting the mortar resulted in lower open porosity of the mortar, which have led to a significant decrease in the permeability of the material compared to the water-wash pre-treatment.

The adsorption and desorption isotherms are required to predict the hygroscopic water content in cementitious materials under changing climatic conditions. It has been shown that hysteresis between the adsorption and desorption isotherms of cementitious materials is significant (Espinosa and Franke, 2006), and so it was for the mortars analysed in this article. Sorption thermodynamics and the particular pore structure of cementitious materials determine the sorption behaviour. Since the pore structure changes during the hydration of cement (Lawrence, 2017), during the drying process (Beaudoin and Tamtsia, 2004) and during chemical ageing (Thomas and Jennings, 2006), it could be expected that it also affects the sorption properties. Determination of sorption isotherms that was performed in climatic chambers showed that the amount of moisture adsorbed was higher for the mortar samples with low porosity. The water vapour was adsorbed by the cement constituent and reacted with the CO_2 supplied to the climate chamber, together with moist air, to produce CaCO_3 . Carbonation is a natural process that occurs in moist air with access to CO_2 , and the highest carbonation rate occurs at 50%–80% RH (Tuutti, 1982). This reaction may result in a greater increase in mass change when comparing the two sorption test methods applied, that is, the climatic chamber method (Figure 2) and the glass desiccators (Figure 3). For example, cement-based mortar reached 6.5% mass gain due to carbonation, compared to dry mass, when measured with the climatic chamber method, and only 4% mass gain when measured in a desiccator. The results obtained in the sorption tests performed in the climatic chambers corroborate the results on cement and ash sorption isotherms reported in Krejcirikova et al. (in press). The sorption isotherm of cement was located significantly above the sorption isotherms of the ashes, so larger mass gains for cement were observed compared to that of any type of ash, regardless of which pre-treatment method was applied. This indicates that sorption ability may be affected by the potential reactivity of cement/ash with water, which is obviously higher for the cement.

In contrast, the sorption isotherms obtained in the tests in the glass desiccators show a slightly different adsorption ability, one that was dependent on the

percentage of cement replacement. Isotherms obtained from desiccators (when the desorption test was performed before the adsorption test) coincided with each other independently of the mortar composition. Similar results were observed in Issaadi et al. (2015) when cement-based mortar was compared with mortar where a proportion of the cement (30%) had been replaced with blast furnace slag. It was reported that the adsorption/desorption isotherms of samples with the same age showed only minor differences between these materials. However, it is not easy to assess the hygroscopic properties of cementitious materials, as in addition to the capillary effect between condensation and evaporation in the pores, according to the Kelvin equation, the chemical water uptake, the drying process and the chemical ageing may affect the observed values.

Summarizing the results achieved by different sorption methods, the observed differences between the isotherms may have been caused by changes in the material structure, which occur as a result of the chemical ageing and carbonation that take place in parallel with the weight gain by water vapour adsorption. Although cement and ash show a different sorption activity (Krejcirikova et al., in press), replacement of cement by 30% of SSA did not lead to any significant effect on the sorption ability of the final product, that is, on the mortar. The ageing of the material and its reactivity with adsorbed water and the carbon dioxide present in the climatic chamber caused differences to be observed between samples containing 0% and 30% of ash. The climatic chamber method was chosen in order to simulate most credibly the indoor environment, where CO₂ is present. It seems that experimentally this is the weakness of using the climatic chamber method for the determination of the sorption properties of cementitious materials. Detailed examination of the carbonation process in the material sample is difficult due to the various factors that affect carbonation rate and the methods used to examine it. The climate chamber method with open CO₂ access is therefore not recommended for assessing cementitious materials if it is required that the measurements should be unaffected by the CO₂ concentration, as was also recommended in Johannesson and Utgenannt (2001) and Pham (2014b).

An effect of the structural changes was also shown in the repeated permeability test in which the dry cup water vapour permeability test was repeated after 1 year. Except for the first dry cup test when samples had been newly cast and dried, the samples were stored for a year in a test chamber with a normal indoor environment and thus came into contact with moisture and CO₂. Comparing the first and the second dry cup test taken 1 year later, the measured permeability decreased for all the samples tested. This is in accordance with the theory of Pham and Prince (2014) that small pores are clogged by calcium carbonate while the distribution of mesopores increases simultaneously.

In general, it can be concluded that partial replacement of cement by SSA has the effect on hygrothermal properties of mortar, especially those properties directly related to mortar structure (porosity) and at higher cement replacement ratios (30%). Cement replacement by up to 10% can be a good compromise of slightly

changed mortar properties and beneficial contribution to CO₂ reduction related to decreased cement consumption.

Conclusion

- The most effective drying was achieved with new samples of mortar prior to all experiments.
- Lower thermal conductivity and higher vapour permeability may be a result of higher mortar porosity due to the larger grain size of SSA compared to cement.
- The thermal conductivity of mortar was reduced by 15% when 30% of the cement was replaced by SSA.
- Sorption was influenced by the test method used. Differences between cement-based and cement-ash-based mortar could be seen when samples were exposed to air containing CO₂.
- The calcium carbonate content was shown to be higher for cement-based mortar compared to cement-ash-based mortar.
- Carbonation of mortar and its consequences must be considered not only in the process of data processing but already in the experimental procedure and time planning. The age of the samples may influence the parameters of cementitious materials considerably.

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Paper III

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The effects of cement-based and cement-ash-based mortar slabs on indoor air quality



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Sink effect

ABSTRACT

The effects of emissions from cement-based and cement-ash-based mortar slabs were studied. In the latter, 30% of the cement content had been replaced by sewage sludge ash. They were tested singly and together with either carpet or linoleum. The air exhausted from the chambers was assessed by means of odour intensity and chemical characterization of emissions. Odour intensity increased with the increased exposed area of the slabs. It did not differ significantly between cement-based or cement-ash-based mortar and neither did the chemical composition of the exhaust air. A significant sink effect was observed when linoleum was added to any of the two slabs examined. The sink effect increased as the exposed area of the slabs was increased. The odour intensity of the mixture of the slab and linoleum was lower than the intensity of odour produced by any of the two materials when tested singly. A plausible explanation for this effect was that the mortar slabs adsorbed the organic acids that were emitted at a high rate from linoleum, mortar being strong base. The same sink effect was also observed when the mortar slabs were exposed together with carpet but it was much smaller because the carpet emitted smaller quantities of acids. The total concentration of organic compounds measured was not appreciably different when the slabs were tested alone or together with linoleum or carpet. Considerable differences in the concentration of organic compounds were however observed when the total concentration of each functional group was calculated and compared.

1. Introduction

The development of building new technologies is currently being driven by the demands of energy conservation, waste management and economic prosperity. In these areas, building development seeks to maintain high living standards and positive socio-economic trends while also seeking to minimize the irreversible destruction of nature. As a result, in recent decades the development of innovative and high-performing building materials has been one of the major drivers for the construction industry. The Industrial Technologies arm of the Research and Innovation Department of the European Commission estimated that 70% of all new product innovation today is based on materials with improved properties [1]. The new materials offer potentially huge benefits for the building industry in terms of cost and performance. At the same time, it must be ensured that the new materials do not create new risks in the form of negative effects on indoor air quality (IAQ) that results in discomfort and a higher risk of health problems. IAQ is one of the major concerns in buildings because it can impact the health, comfort, well-being, and cognitive performance of building occupants [2]; [3]. Short and long-term exposures of building occupants to

pollutants emitted from building materials or pollutants produced due to chemical transformation of the emitted pollutants can produce sensory nuisance (e.g. Ref. [4]) and can lead to the development of building related health symptoms such as fatigue, eye irritation, itchiness, nose and throat irritation, nausea, headaches, dizziness, skin irritation, rashes [5]. In particular cases, chronic and severe diseases can be caused or exacerbated. These include asthma, reproductive impairment, disruption of the endocrine system, cancer, impaired child development, birth defects, and immune system suppression [5]. Consequently, new and/or alternative materials should always undergo a comprehensive assessment process, including an examination of the emissions of potentially toxic compounds. These aspects are not typically the concern of the building industry and are not considered exhaustively when new materials are being developed.

Among many new alternative building materials there is an ash mortar. In ash mortar, fly ash is used to partially replace cement. Mortar that is a structural material itself, or is used in concrete production, usually contains cement, sand and water. Cement is a crucial ingredient of the mortar and acts as a binder. Cement manufacturing is economically and energetically a very demanding process. About 5%–7% of all

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global anthropogenic carbon dioxide (CO₂) emissions are released from plants manufacturing cement and 900 kg CO₂ is emitted to the atmosphere during production of one ton of cement; this is a nearly 1:1 ratio [6]. Any improvements in cement production will thereby bring tangible effects and there have been significant steps towards improving the sustainability of concrete production by finding cement substitutes [7]. Cement is additionally the second most consumed substance in the world by weight, second only to water, with global cement production at 4.2 billion tons in 2016 [8]. It is estimated that annual concrete consumption is at 3.8 billion m³ worldwide (as stated by Cement Association of Canada). Thus even a few percent of cement substitution by an alternative material would bring considerable benefits. This substitution will additionally reduce the need to mine the virgin raw material. Among other benefits there is also a reduction in the need for landfilling.

For decades the industry incorporated fly ash from coal combustion power stations as a supplementary cementing material [9]. However, very limited information was available on emissions from mortar containing fly ash. A Danish study [10] compared the emissions from cement-based concrete and cement-ash-based concrete. The results showed that concrete that was cast in a mould that had been sprayed with mineral-oil emitted hydrocarbons which could be eliminated by using vegetable-based oils, while concrete containing fly ash from coal combustion power plants emitted ammonia. The emission rates of ammonia were rather low, and they were not thought to create any considerable risk of reduced indoor air quality. Actually, it was also shown that the cement-based concrete emitted ammonia. Neither of the two concrete types were sources of amines, alcohols or aldehydes. The report from the project mentioned that sensory assessments were made of the emissions of cement-based concrete with an area of 0.4 m². They showed that they produced moderate to weak odour intensity that decreased over time.

Besides the benefit of cement replacement, fly ash acquired from coal combustion power stations might possess some air cleaning properties similar to those of activated carbon [11], and [12] investigated whether fly ash from coal combustion could be used as an adsorbent material for toluene vapour. The experiments showed that coal fly ash may indeed act as a possible adsorbent of toluene and more generally, of other organic gases and vapours, but only after suitable activation treatment, which specifically included particle aggregation and thermal activation. These processes resulted in the coal ash acquiring adsorbing properties that were comparable with the usual but more expensive activated carbon. Whether adding fly ash that has undergone activation treatment to cement mortar can result in the product having air cleaning properties has not yet been investigated.

Only a few experiments have examined the interaction between mortar and air pollutants. Most of the them examined the possibility of air cleaning by adding photocatalytic additives, specifically TiO₂, to concrete (e.g. Refs. [6,7,13–16]). Some studies focused on the interaction between cement-based concrete with various pollutants such NO_x, CO₂, and SO₂ (e.g. [17–22] [18], examined the interaction of three mortar mixtures with volatile organic compounds (VOCs). Samples included common cement mortar, a dehumidifying salt resistant mortar and a cement-free mortar containing a natural binder (pozzolana). The sorption ability of the mortar was examined by injecting a mixture of VOCs (methanol solution composed of several VOCs: benzene, heptene, heptane, o-m-p xylene, toluene, ethyl benzene, cumene, ethylene glycol monobutyl ether and diethylene glycol monobutyl ether acetate, carene, isolongifolene) into the steel chamber, where a specimen of cement mortar was present. The results revealed that all three mortar types reduced the total concentration of VOCs (TVOC) during a 24-h test; during this period the chambers were flushed with nitrogen at the rate of 20 cm³/h. Specifically, in the case of common mortar, the TVOC concentration decreased from an initial concentration of approximately 4500 µg/m³ to 1000 µg/m³. In addition, the mortar containing natural pozzolana caused the largest reduction in TVOC concentration

compared to the other two mortars. This effect could be due to the different composition of the mortars and the use of a natural material that affects the final structure of the mortar, as the final product has higher porosity: the pictures from the scanning electron microscope revealed that a greater superficial area was available for adsorption [18]. postulated that various reductions of TVOC in the presence of mortars can be caused not only by differences in porosity and in the physical characteristic of the mortars but also by chemical reactions. This postulation was based on results that showed that the VOCs detected in the presence of mortar containing natural pozzolana differed from those detected in the presence of other mortars. However, no details of the examinations and procedures were provided in the conference paper by Ref. [18]. There are also studies that investigated interaction of mortar with outdoor pollutants under conditions typical for outdoor air such as [10,17,23,24]. As they are outside the scope of the present work they are not described here though it is worth mentioning that they showed that mortar has the potential to reduce levels of NO_x.

The overall objective of the present work was to compare mortar samples with standard composition (cement-based mortar) with alternative mortar samples in which cement had been partly replaced by sewage sludge ash (cement-ash-based mortar). The study formed a part of the ZeroWaste initiative at the Department of Civil Engineering at the Technical University of Denmark (DTU) [25] http://www.byg.dtu.dk/innovation_og_myndighedsbetjening/zerowaste-byg). The purpose of this initiative was to examine and potentially develop building materials in which natural raw materials are replaced by secondary resources, including waste materials. Besides comparing the quality of air polluted by emissions from two types of mortar samples, it was additionally examined whether indoor air quality would change if mortar slabs were present together with either linoleum or carpet, two typical indoor floor surface materials. The intention was to determine whether such concrete slabs exhibit any air cleaning properties. The two specific research questions investigated in the present experiments were thus as follows: (1) Do emissions from mortar with and without ash have the same impact on perceived odour intensity? and (2) Does the odour intensity change when the mortar slabs are present together with samples of carpet or linoleum? Sensory assessments and chemical measurements were used to answer these questions. The former is supplementary to the latter especially as it is difficult to predict the impact of pollutants emitted by materials indoors on air quality as it is perceived by occupants of buildings [26,27].

2. Methods

2.1. Materials

Two mortar mixtures were cast according to the standard DS/[28]; a standard cement-based mortar made of a cement-sand mixture (further abbreviated as CM) and a cement-ash-based mortar (abbreviated as AM) where 30% of the cement content had been replaced by sewage sludge ash originating from the incineration power plant located nearby in Copenhagen, Denmark. Newly cast mortar panels were air-dried at 45 °C after hardening for 28 days in a water bath, and afterwards stored in airtight foil; they were unpacked prior to being loaded into test chambers made of glass.

Linoleum (abbreviated as Li) and carpet (abbreviated as Ca) were chosen as two typical materials representing indoor wall-to-wall floor coverings. Both of them are typical materials used indoors and both emit elevated concentration of VOCs into the air. Their emissions can also participate in chemical transformations that result in new indoor air pollutants [3,29–36]. The linoleum (with coloured patterns) used in the present experiment was bought in the early 2000, cut into pieces and used in many experiments [14,29,34,37–40]. It had never been installed on the floor in a building. Between experiments, the samples of linoleum were stored on shelves in a well-ventilated laboratory,



Fig. 1. A subject inhaling the air from a diffuser above the glass chamber, which was covered with aluminium foil to prevent subjects from identifying the pollution source (1a) and experimental set up and air sampling for the chemical measurements (1b).

unpacked. The carpet used in the present experiments was a tufted bouclé (100% polyamide fibres and latex backing) that had been installed on a floor and used for about 20 years in an office building, removed in the mid-1990s in connection with other experiment [41] and later used as a source of indoor air pollution in many laboratory experiments (e.g. Refs. [3,42]). When not used in the experiments, the samples were stored on shelves in the laboratory, unpacked, as were the samples of linoleum. During experiments, the samples were stapled back to back so that only the front side was exposed to the air.

Immediately prior to each experiment, all the material samples were conditioned in the preparation room located in front of the test chambers by exposing them to typical indoor conditions for a week in order to bring the samples into equilibrium with the indoor temperature and relative humidity.

2.2. Experimental facilities

The experiments were carried out in the twin stainless steel climate chambers at DTU [43], Fig. 1. Each chamber had a floor area of 9 m^2 , a height of 2.5 m and a volume of 22.5 m^3 . They were ventilated using underfloor air distribution that supplied 100% outdoor air, with exhaust outlets in the ceiling. The chambers were primarily designed for air quality experiments and could provide temperatures from $10 \text{ }^\circ\text{C}$ to $40 \text{ }^\circ\text{C}$ and relative humidity from 10% to 90%. A high air exchange rate could be achieved by underfloor ventilation, up to 50 h^{-1} .

Seven ventilated 200 L glass chambers described in detail by Ref. [44] ($40 \times 50 \times 100 \text{ cm}$) were placed in the stainless steel chambers, 3 in one chamber and 4 in the other one. These chambers had been used in many other experiments to characterize the emissions from materials, using a so-called small-scale setup [45,46]. The samples of the materials tested in the present experiments were placed inside these

chambers. The chambers were made of glass glued together on metal support racks. Two ventilators were attached on the top of each glass cover to ensure that the chambers were well ventilated. The air was extracted via a diffuser allowing for sensory and chemical measurements of the air exhausted from the chamber. The samples of materials were placed in the inner part of the chamber on a stainless steel rack (Fig. 1b). Mortar slabs were placed with the flange on the bottom of each glass chambers while linoleum or carpet was attached to the metal rack placed inside the chamber. The samples were placed with some distance between each so that the air could flow freely around them. A smoke test was performed to confirm that the air was well mixed in the fully loaded glass chambers.

2.3. Experimental conditions

The steel chambers were ventilated with a maximum outdoor airflow resulting in the outdoor air change rate of 50 h^{-1} . The air temperature was set to $23 \text{ }^\circ\text{C}$. Relative humidity was not controlled and varied during experiments between 13% and 32%. The glass chambers were ventilated with the air supplied to the steel chambers. The inlet airflow was set to be about 0.9 L/s and the air velocity at the top of diffuser in the glass chamber where the sensory and chemical measurements were performed was about 0.2 m/s .

The loading of materials in the glass chambers were designed in accordance with the Nordtest method described in NT Build 482 Report [47]. The method defines loading factors for specific surface areas with respect to the dimensions of a model room. Based on the loading factors for a model room (Table 1) and the airflow in the chamber, the total surface areas of the materials exposed were calculated to be 1.4 m^2 , 1.9 m^2 and 2.8 m^2 for the mortar slabs. The area of 1.4 m^2 was considered as an initial loading of the mortar slab that represents a floor or

Table 1

Loading of materials in the present experiments; CM = cement mortar; AM = cement-ash-mortar; Li = linoleum; Ca = carpet.

Material loading in glass chamber [m^2]	Area specific air flow rate q [$\text{m}^3/\text{h m}^2$]	Model room		Material
		Loading factor [m^2/m^3]	Surface area [m^2]	
1.4	2.4	0.420	7.1 ^a	CM, AM, Li, Ca
1.9	1.8	0.571	9.6	CM, AM
2.8	1.2	0.841	14.2	CM, AM

^a Surface area of 7 m^2 represents floor/ceiling area in the model room based on the Nordtest method NT Build 482.

Table 2

Experimental plan including material set up and loadings; CM = cement mortar; AM = cement-ash-mortar; Li = linoleum; Ca = carpet.

Experimental matrix								
Mortar loading [m ²]	CM	CM + Li	CM + Ca	AM	AM + Li	AM + Ca	Li	Ca
1.4	•	•	•	•	•	•	•	•
1.9	•	•		•	•			
2.8	•	•	•	•	•	•		

ceiling area in the model room. The maximum exposed surface area of 2.8 m² was determined with respect to the capacity of the glass chambers – there was no room for more material. Mortar was tested with carpet under two mortar loadings, compared to three loadings in the case with linoleum, because of limited number of the available experimental days being the consequence of limited resources to perform this study. For the carpet and linoleum a loading of 1.4 m² was used, corresponding to the floor area in the model room, as indicated above. All 18 conditions tested in the present experiments are shown in Table 2.

In one of the glass chambers, 2-propanone was evaporated passively so that its concentration was constant at about 80 ppm; the concentration was measured using an Innova 1312 gas monitor. According to [48]; this concentration is predicted to produce a strong odour (as shown in the Supplementary Material (SM2), subjects in this experiment also assessed that this concentration is producing strong odour). 2-propanone exposure was used as a reference condition to examine whether any changes in the performance of the sensory panel performing sensory assessments occurred during the course of experiment.

All the glass chambers were covered with aluminium foil during the experiments so that their content was invisible for the subjects performing the sensory assessments. The location of the materials in the chambers was randomly changed during the course of the experiments to avoid any systematic errors.

2.4. Sensory panel

The sensory panel consisted of twenty-five subjects (13 males and 12 females). They were recruited through advertisements at the university campus. They were 22–38 years old, all university students, non-smokers, and not suffering from asthma, allergies, or other chronic diseases. The subjects judged themselves to be fit and healthy. They participated voluntarily in the experiment. The subjects were asked not to eat spicy food and not to use perfumes during on any of the days of the experiment.

2.5. Sensory measurements

The subjects assessed odour intensity, the acceptability of the air quality, air freshness, pleasantness and nose irritation. Only the ratings

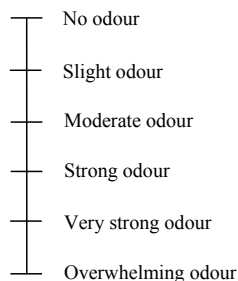


Fig. 2. Odour intensity scale. Once the ratings were performed the scale was coded as follows: 0 – No odour, 1 – Slight odour, 2 – Moderate odour, 3 – Strong odour, 4 – Very strong odour, 5 – Overwhelming odour.

of odour intensity are presented in the present paper and the reason for this is provided later. The ratings were made using scales printed on separate sheets of paper. The odour intensity scale [49] shown in Fig. 2 was used to obtain sensory measurements of odour intensity. The subjects were instructed on how to perform sensory evaluations and had an opportunity to practice the assessments before the actual experiments.

2.6. Chemical measurements

The air used in the chemical analysis was withdrawn from the glass chambers through sorbent tubes inserted into a diffuser perpendicular to the direction of air flow; steel tubes containing Tenax TA sorbent were used (Fig. 1b). Double sampling was made; the volumes sampled were 3 L and 4 L. The airflow rates through the tubes were 0.1 L/min and 0.08 L/min respectively; they were controlled by calibrated pumps. A 3-L sampling was additionally made of the background air in the chamber. Blanks were made and analysed, too.

The samples were analysed by an external certified laboratory. The sampling tubes were desorbed in an automated thermal desorption/purge and trap injector. The airborne substances adsorbed on Tenax TA were analysed by TDS-GC-MS according to ISO 16000-6. After transferring to a non-polar capillary column, the trapped compounds were separated in a gas chromatograph and detected in a mass spectrometer. Identification of compounds was achieved using standard mass spectra libraries (NIST, Wiley). The compounds identified were quantified against pure reference compounds covering volatile organic compounds (VOCs) from C5 to C22. Substances in the range of C6 to C16 were reported as VOCs, the more volatile ones as very volatile organic compounds (VVOs), and those eluting after C16 as semi-volatile organic compounds (SVOCs). The concentrations were calculated as toluene equivalents with a lower reporting limit of 1 µg/m³.

In the conditions in which cement-ash-based mortar samples were present there could have been ammonia emissions due to the ash processing [50] [51]; [10]. Two conditions with such samples at the highest mortar loading of 2.8 m² were therefore examined for ammonia according to the guidelines relevant for organic recycled materials and ash-made concrete as defined by the National Institute for Occupational Safety and Health (NIOSH). The method is based on a solid sorbent tube, sulfuric acid-treated silica gel, and spectrophotometry. The accuracy of the method is not available.

2.7. Procedures

The sensory evaluations of the air extracted from the chambers with samples of mortar, flooring materials and their combinations present, an empty chamber and a chamber containing 2-Propanone were carried out on eight non-consecutive days in March and April 2015. The glass chambers in the stainless steel chambers were loaded with the tested materials on the day prior to each experimental session and sealed with an aluminium emission-free tape. Material samples were conditioned for about 20 h prior to the assessments or to chemical sampling. During sensory assessments, the subjects assembled in the ventilated hall adjacent to the stainless steel chambers. They were then called one-by-one by name and asked to perform an evaluation of the air extracted through the diffuser from one of the seven chambers. After entering the chamber, they approached the diffuser and inhaled the air exhausted from the chamber through it. Only one inhalation was made, after which they rated odour intensity, the acceptability of the air quality, irritation, freshness and pleasantness of the air. Then they left the chamber and took a 1–3 min break in the ventilated space before the next evaluation. The subjects performed 9 evaluations on one day and a total of 72 evaluations during the eight-day experiments. Besides assessments of the air extracted from the chambers they also assessed the air in each steel chamber. The order in which the evaluations were made was randomized for all subjects.

Chemical sampling was performed on the same samples and with an identical chamber setup one year after the sensory experiment. In the meantime, the material samples had been wrapped and stored. Identical procedures for conditioning the samples as in case of the sensory assessments were applied.

2.8. Statistical analyses

Statistical software R version 3.3.1 [52] was used to analyse the results of the sensory assessments. A Linear Mixed Effects (LME) model [53] was used to analyse the influence of the different types of mortar, the amount of mortar present (loading) and the presence/absence of linoleum/carpet on the odour intensity assessed by the subjects. Type and loading of mortar and presence of pollution source were treated as fixed effects (with interactions) in the model. Subjects were treated as a random factor to account for a repeated-measures design. Inspection of Quantile-Quantile plots (QQ-plots) was used to evaluate the Normality of the model residuals. As the model residuals turned out to deviate from a Normal distribution, the data were log-transformed before analysis. In addition, pair-wise comparisons were made using the Wilcoxon matched-pairs signed-ranks test to compare linoleum and carpet alone and in combination with mortar, and to investigate differences between mortars at a specific loading. The level for rejection of the Null Hypothesis was set at $P = 0.05$ (2 tail).

3. Results

3.1. Sensory assessments

The odour intensity increased linearly as a function of the logarithm of the material loading, following the function established by Ref. [54] (Fig. 3).

The results of the analysis of the Linear Mixed Effects (LME) model are shown in Figs. 4 and 5. They show that when mortar slabs were present alone in the chambers there was no significant difference in the mean odour intensity produced by either cement-based mortar or cement-ash-based mortar at the same loading. As the loading increased, the odour intensity increased and the increase of odour intensity with the mortar loading was statistically significant ($p < 0.001$). Addition of linoleum or carpet to mortars at the lowest loading level of 1.4 m^2 significantly increased the odour intensity ($p < 0.05$). The odour intensity of cement-ash-based mortar with linoleum was significantly higher ($p < 0.05$) at the loading levels of 1.9 m^2 and 2.8 m^2 compared to cement-based mortar with linoleum. The similar was observed for the combination of carpet with cement-based mortar and cement-ash-based mortar, significant differences were observed for both studied loadings, specifically significant difference ($p < 0.05$) for 1.4 m^2 loading of mortars and significant difference ($p < 0.001$) for 2.8 m^2 loading of mortars. Increasing the loading of mortars with linoleum

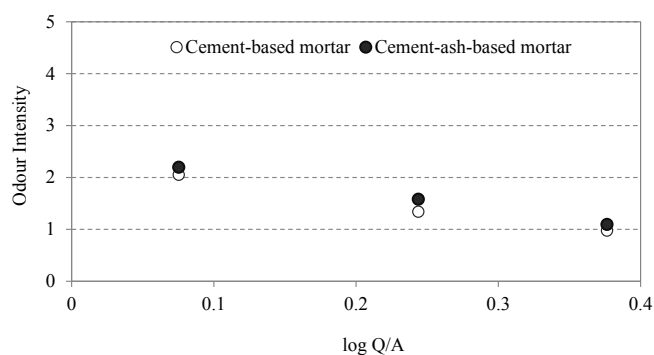


Fig. 3. Exposure – response relationship between the logarithm of the ventilation rate to loading of cement-based mortar (CM) and cement-ash-based mortar (AM) ($\log Q/A$) and the perceived odour intensity.

significantly decreased the perceived odour intensity ($p < 0.05$). Increasing the loading of mortars with carpet did not change the odour intensity in the case of the combination of carpet and the cement-ash-based mortar but significantly decreased the odour intensity when carpet and cement-based mortar were both present. A detailed summary of the results of the LME model analyses and on the acceptability of the perceived air quality are presented in the [Supplementary Material \(SM1\)](#), which also includes the results of the assessments made on the acceptability scale and show the same trends as for the ratings of odour intensity.

The [Supplementary Material \(SM2\)](#) also presents the sensory assessments of 2-Propanone (Acetone), which showed no changes in these ratings during the eight-day long experiments.

3.2. Chemical measurements

[Table 3](#) shows the results of the GC-MS analyses, listing the compounds detected with a toluene equivalent concentration higher than $1 \mu\text{g}/\text{m}^3$. The results presented in [Table 3](#) are from the 3-L samples; results based on 4-L sampling (presented in the [Supplementary Material \(SM3\)](#)) revealed that the compounds detected were the same but they showed lower concentrations for most of the compounds compared with the 3-L samples, suggesting that break-through had occurred. [Table 3](#) shows that any differences in types and concentration of pollutants emitted by cement-based and cement-ash-based mortars were negligible. In the case of the linoleum, the measurements showed that it was a strong source of organic acids, many of which occurred at fairly high concentrations, often close to their odour thresholds. The results presented in the table show that the concentrations of these acids decreased when linoleum was present in combination with cement-based and cement-ash-based mortars. In the case of the carpet, [Table 3](#) shows that it was a moderate source of acids, alcohols and aldehydes. When it was present in combination with the mortars, the concentration of acids decreased as in the case of linoleum and the concentrations of other compounds remained unchanged. [Table 3](#) shows no marked differences in the concentrations of VOCs, TVOCs and SVOCs for the conditions analysed. However, differences were found when the concentrations of compounds constituting different functional groups were aggregated and compared, especially as regards the organic acids. The graph in the [Supplementary Material \(SM4\)](#) shows these differences.

Chemical analyses of the cement-ash-based mortar samples examining ammonia emissions were performed at the highest loading of the mortar (2.8 m^2). They were performed when mortar was present alone and in combination with linoleum. In both cases the concentration was below the limit of detection for ammonia, which was $0.030 \text{ mg}/\text{m}^3$ in 40 L of sampled air.

4. Discussion

Sensory assessments of odour intensity did not suggest differences in emissions between cement-based mortar and cement-ash-based mortar (Figs. 3–5). However, chemical measurements ([Table 3](#)) showed that the TVOC concentration was higher for the cement-based mortar than for the cement-ash-based mortar at the highest loading (2.8 m^2). The reason for the difference was the high concentration of triethylene glycol. Neither of the mortars is expected to emit this compound. This was confirmed by the results of measurements performed at other loadings and the mixtures of mortars with linoleum and carpet where triethylene glycol could not be detected. It is possible that the presence of triethylene glycol was due to the cleaning of the glass chambers that took place before new loading was placed in the glass chamber, triethylene glycol being a residue of the detergent used for cleaning the glass surfaces. It would then be fair to conclude that adding sewage sludge fly ash to mortar does not have a measurable effect on the VOC emissions from a cement-based mortar slab.

The odour intensity increased when linoleum was placed together

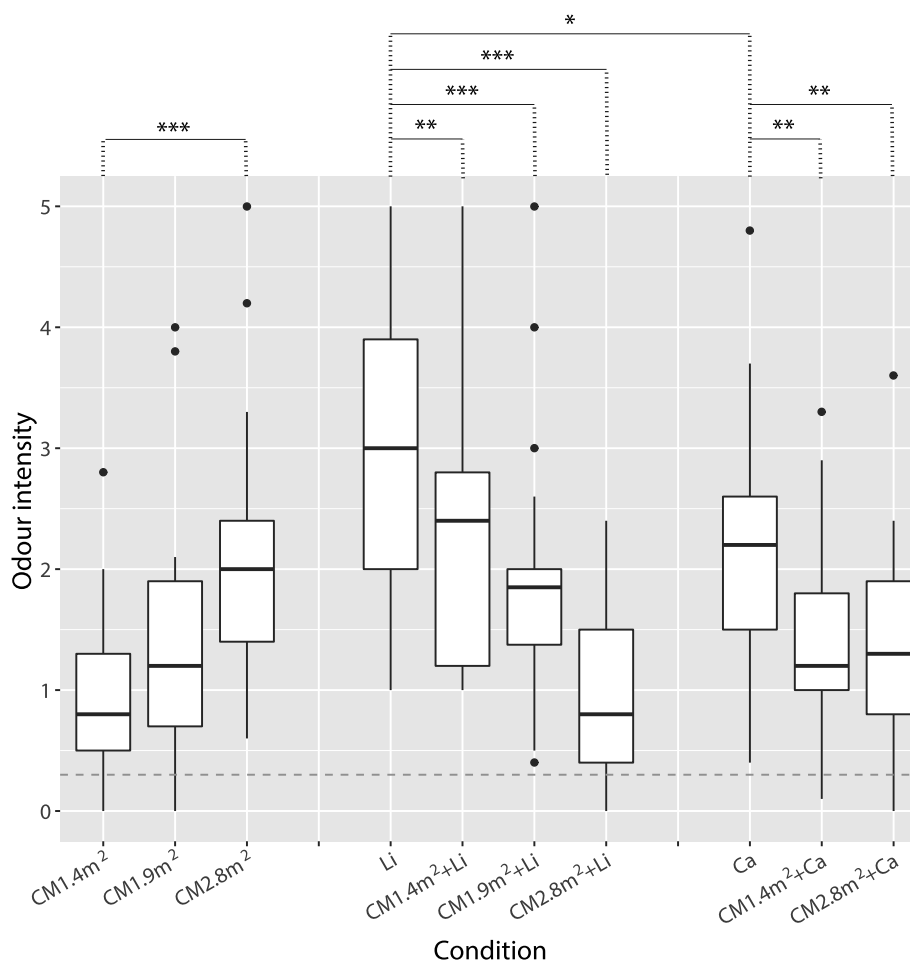


Fig. 4. Boxplots presenting assessment of odour intensity on the air extracted from the chambers containing cement-based mortar slabs (CM), linoleum (Li), carpet (Ca) and their mixtures. Black dots show outliers while dashed line presents the median of odour intensity of the air extracted from the empty glass chamber (OI = 0.3). Asterisks indicate the results of pairwise comparisons examined using Wilcoxon signed-rank test, where * indicates $0.01 < p < 0.05$, ** indicates $0.001 > p > 0.01$ and *** shows that $p < 0.001$. It should be noted that the box plots present raw data while the statistical analyses were made on the log-transformed data.

with the cement-based and the cement-ash-based mortar. But then it decreased when the loading of the mortars was increased and was even lower than when the mortars alone were present. One possible explanation for the observed phenomenon could be that the mortars adsorb the pollutants emitted from linoleum. Table 3 shows that the mortars are a particularly strong sink for organic acids, which are emitted in fairly large quantities from linoleum. The sink effect can be explained by the fact that the mortars represent a strong base, which attracts acids. They have a particularly high pH when freshly cast [57] though with time, as the mortar matures, its alkalinity decreases and pH neutralizes due to a carbonation process that forms calcium carbonate. This suggests that the potential for adsorbing organic acids could decrease with time. However, this was not observed in the present experiments. The sensory measurements were performed a few weeks after the mortars were cast, while the chemical measurements were carried out one year later, and both indicated a strong sink effect. In future experiments, it would be interesting to examine how long mortars maintain their ability to adsorb acids.

The aging of mortars produces other changes in their structure due to chemical reactions and drying [58,59]. showed that these processes result in micropores being clogged while mesopore structure likely to expand due to the cracks that form during carbonation. These processes may increase the potential area for adsorption even though the pH has decreased. It may thus be postulated that the sink effect observed directly after casting the mortars was due to their basicity and the sink effect observed one year later, when the chemical measurements were

made, was due to both their porosity and basicity, but this hypothesis cannot be verified by using only the present result. In the future experiments, it would be useful to study further the mechanisms causing the sink effects and how long they last. The observed sink effects may also change depending on the way the indoor surfaces are finished. Information on these sink effects and their mechanisms may have considerable practical implications.

When the magnitude by which odour intensity was reduced in the combined exposure of mortars with linoleum is examined, it can be concluded that it is rather unlikely that the adsorption of pollutants was the only mechanism that was responsible. For example, it could also be that the odour produced by the mortars was masked by that of linoleum or that the adsorption of compounds on the mortar surface could have reduced emissions by blocking or clogging the mortar pores. A possible explanation for the reduced odour intensity in the combined exposure of mortars with linoleum could also be the compensation or subtraction of odour intensities, which is a specific case of hypo-addition of two odour intensities [60]. Future experiments should closely examine and describe these processes to further elucidate the results observed in the present study.

Based on chemical measurements, linoleum is a strong source of organic acids while carpet emits fewer acids (Table 3). This explains why the sink effect was much smaller in the case of the combined exposure of mortars with carpet. It should be noticed that the sink effect was seen both for the cement-based and the cement-ash-based mortar, which suggests that adding fly ash did not change the sorption

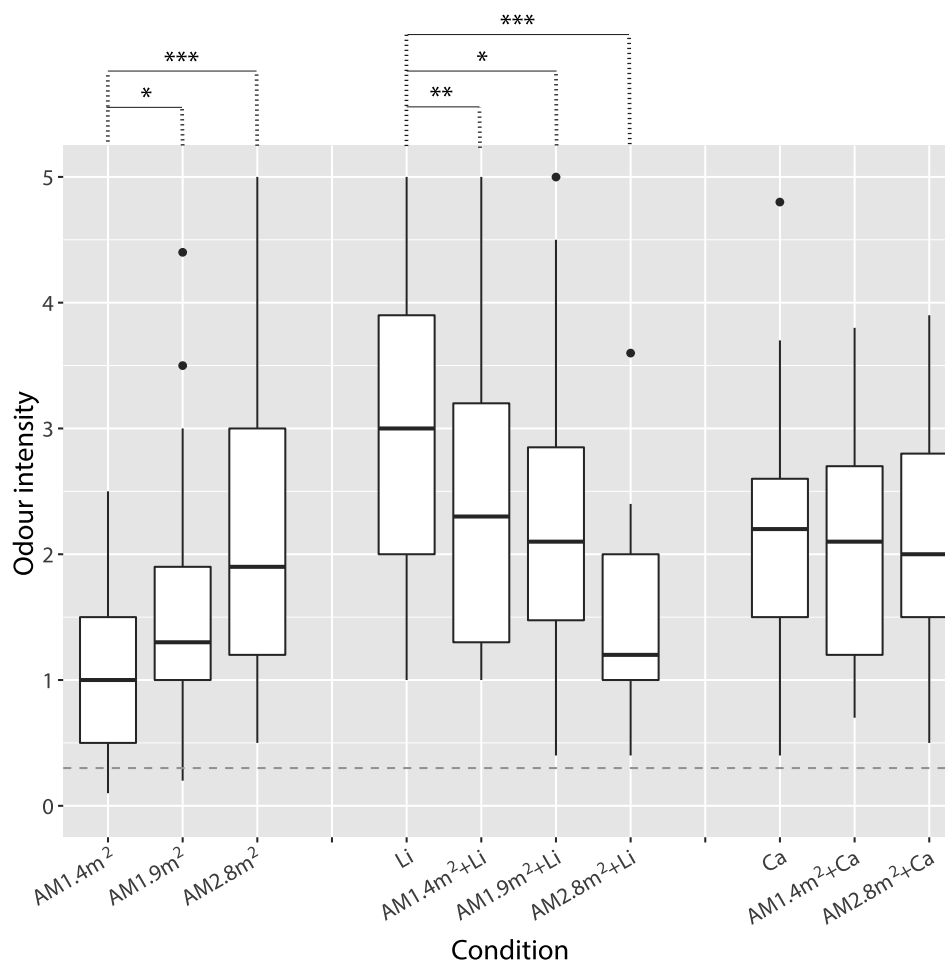


Fig. 5. Boxplots presenting assessment of odour intensity on the air extracted from the chambers containing cement—ash-based mortar slabs (AM), linoleum (Li), carpet (Ca) and their mixtures. Black dots show outliers while the dashed line presents the median of odour intensity of the air extracted from the empty glass chamber (OI = 0.3). Asterisks indicate the results of pairwise comparisons examined using Wilcoxon signed-rank test, where * indicates $0.01 < p < 0.05$, ** indicates $0.001 > p < 0.01$ and *** shows that $p < 0.001$. It should be noted that the box plots present raw data while the statistical analyses were made on the log-transformed data.

properties. The above comparisons provide an independent verification and reproducibility of the observed sink effect for the cement-based mortar.

The sensory assessments showed that linoleum produced the strongest odour among all conditions tested (Figs. 4 and 5). It was higher than the intensity of odour produced by the carpet, cement-based and cement-ash-based mortars. However, the TVOC concentration did not validate the presence of such considerable differences and showed that the emissions from the cement-based mortar were actually the highest. Taking these results into account it can be concluded that pure chemical measurements may not always provide information on the potential effects of material emissions on air quality as it is perceived by humans. In addition, the results presented in Table 3 imply that there are considerable limitations on aggregating the concentrations of VOCs measured or integrating the signal from gas chromatography and expressing the concentration of all pollutants as the Toluene equivalent concentration. The result of these procedures, the TVOC concentration, may not be able to predict the effects on humans, as was pointed out by Ref. [44].

It is worth noting that the present results show the benefits of chemical measurements and support the need for them. They show that detailed analysis of pollutants is worthwhile because a clear difference between the concentrations of individual pollutants and the sum of concentrations of functional groups can be seen (Table 3). For example, in the case of linoleum, high levels of organic acids were measured and in the case of the carpet, aldehydes and alcohols were measured at

levels that were similar to those reported in other studies [3,30,31,33,35,36,61]. These compounds have low odour thresholds as compared to the emissions from cement-based and cement-ash-based mortars [62]. This can explain why the emissions from linoleum and carpet produced the highest odour intensity (Figs. 4 and 5). Mortar samples, which are composed of mainly inorganic components, which were not measured in the present experiments, were mostly sources of iso/cyclo-alkanes, which can be considered to be without perceptible odour. The origin of the iso/cyclo-alkanes was not identified, but based on the Green Concrete study [10], the mineral oil sprayed into the mould used to cast each slab may be a source of hydrocarbons, a functional group of compounds containing alkanes, cycloalkanes and others. Table 3 shows differences between the aggregated concentrations of pollutants from different functional groups, suggesting that if integrated indexes are based on chemical measurements they should differentiate between functional groups of pollutants rather than integrate all pollutants “across the board” as is conventional when calculating TVOC concentration (see e.g. Ref. [63]). This approach was proposed by Ref. [64] when they defined the limits for TVOC concentration to avoid discomfort based on the measured VOC levels in existing buildings and proposed limits on indicators created by aggregating the concentrations of VOCs for each specific group of compounds.

As described in the Methods section, the 3 L and 4 L samples were taken during the chemical measurements. The analyses of both samples show that the concentration of pollutants in 4 L samples was in general

Table 3
Concentrations of compounds emitted from the cement-based mortar (CM), cement-ash-based mortar (AM), linoleum (Li), carpet (Ca) and their mixtures; the results are from the 3 L samples and the concentrations are toluene equivalents in µg/m³. Odour thresholds (OT) compiled by Ref. [55] or determined by Ref. [56]; (marked with *) are presented as well.

Materials	Concentration range µg/m ³ (3-L sampling)							OT		
	CM 2.8 m ²	AM 2.8 m ²	Linoleum (Li)	CM 1.4 m ² + Li	CM 2.8 m ² + Li	AM 2.8 m ² + Li	Carpet (Ca)		CM 2.8 m ² + Ca	AM 2.8 m ² + Ca
ALCOHOLS										
1-Dodecanol					2		3			100
1-Ethoxy-2-propanol					1		3			
2-Ethyl-1-hexanol					2		7			115*
Benzyl alcohol					1		3			
n-Butanol	4	3	8	8	4	4	4	4	4	427/21*
Phenol				1						
Triethylene glycol	270	14								
Trimethylsilanol	1									
Sum Alcohols	275	17	8	9	4	4	17	13	4	
ALDEHYDES										
Benzaldehyde		2	2	2	2	2	5	2	2	186
trans-2-Decenal			3							2
Dodecanal							2			
Pentanal								3		22
n-Decanal		1	3	3	2	7	3	3	3	6
n-Hexanal	2	1					2	5		58
n-Nonanal		2	7	5	3	5	7	4	4	13
Octanal			2		1		3	2		7
Sum Aldehydes	2	6	17	10	8	14	22	19	9	
ORGANIC ACIDS										
Acetic acid	15	8	63	16	21	13	119	20	31	363/16*
Butanoic acid			11		2					14
Decanoic acid (Nonanoic acid)			2	1	2	1	3		1	63
Formic acid			76						15	54954
Heptanoic acid			11		2					148
Hexanoic acid			41	4	5	3	5	2	1	60/3
Isobutyric acid			2							
Lactic acid		1				1		4	2	
Nonanoic acid			5		1		2			13
Octanoic acid			15		3	1	2			24
Pentanoic acid			13							20
Propanoic acid			51		5					110
Sum organic acids	15	9	290	21	41	19	131	26	50	
ALKANES										
2-Methylpentane (3-Methylpentane) (Isohexane)								154		
Methylcyclopentane								36		
Cyclohexane								5		77625
C6 (Hexane)								36		79433/5690*
C15 (Pentadecane)		4		4	3	3		2	2	
C16 (Hexadecane)		3		3	2	3	3	2	3	
Hexamethylcyclotrisiloxane		2	2	2	1	2	1	2	1	
Sum alkanes	0	9	2	9	6	8	4	237	6	

(continued on next page)

Table 3 (continued)

Materials	Concentration range $\mu\text{g}/\text{m}^3$ (3-L sampling)							OT		
	CM 2.8 m ²	AM 2.8 m ²	Linoleum (Li)	CM 1.4 m ² + Li	CM 2.8 m ² + Li	AM 2.8 m ² + Li	Carpet (Ca)		CM 2.8 m ² + Ca	AM 2.8 m ² + Ca
Sum other iso/cyclo-alkanes:	129	152	4	138	94	110	38	84	95	
OTHER COMPOUNDS										
Acetone	3	3			3		4	23		34674/11300*
N-Methyl-2-pyrrolidone			2							
gamma-Nonalactone			2		1		2			933/82*
n-Butyl acetate										
Benzothiazole			2				3			
Dicarboxylic acid ester			2	2		1	1		1	
Dibutyl ether	2	1	<1	2	1		1	2		5888/1340*
Toluene			1				2			
Sum other terpenes:										
Sum VVOC (< C6):	4	4	76	<1	4	<1	5	179	15	
TVOC (C6-C16):	461	194	251	191	154	156	222	225	150	
Sum SVOC (> C16):	<1	<1	<1	<1	<1	<1	<1	<1	<1	
TVOC Toluene equivalents (ISO 16000-6):	243	90	42	120	36	62	199	81	46	

lower, suggesting breakthrough. This is why only the results for the 3 L samples were presented in Table 3. Despite the breakthrough, the trends of the results of the chemical measurements in the different conditions were the same when the analyses of 3 L and 4 L samples were compared (see Supplementary Material (SM3)), both showing that organic acids were removed by the mortar slabs.

The relative humidity was not controlled in the present experiments. This could bias the assessments of acceptability of air quality [65]. Odour intensity was therefore used as a major sensory outcome, as the results of [65] show that perception of odour intensity is not affected by varying temperature and relative humidity of the inhaled air; similar approach was used by Ref. [66]. Although the ratings of acceptability were not used as the major sensory outcome, they generally corresponded to the ratings of odour intensity (see Supplementary Material (SM1)).

The present results show that building materials should not only be considered as pollution sources [46], but also in some cases as potential air cleaners. A similar conclusion was put forward by Ref. [67]; who showed that unpainted gypsum walls can considerably improve perceived air quality, while [68] showed that clay plaster can act as a buffer for ozone.

Even though the present results do not show any large difference between cement-based and cement-ash-based mortars the potential risks for the environment and for health of the ash content, e.g. leakage of heavy metals, should also be investigated and considered before mortars with fly ash can be considered harmless.

5. Conclusions

- There were no differences in sensory emissions or chemical emissions between cement-based mortar and cement-ash-based mortar at the same loading.
- Odour intensity increased as the loading of cement-based mortar or cement-ash-based mortar increased.
- Both cement-based mortar and cement-ash-based mortar were shown to be significant sinks for organic acids.
- Cement-ash-based mortar is not a source of ammonia emissions at a detectable level.
- TVOC is not a good indicator of the sensory effects of emissions from materials, but the sum of VOCs of functional groups can be considered as a crude indicator of potential sensory effects.
- Future experiments should investigate the long-term adsorption capacity of the mortars investigated in the present experiments for acids and other pollutants and should validate the present laboratory findings in real scenarios.

Declaration of interest

None.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.buildenv.2018.03.011>.

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Supplementary material SM1 – Tables

Table 1 *Summary of the fixed effects from the LME model with the following model syntax (Pinheiro et al., 2017):**odour intensity ~ material [CM, AM] * load [low, medium, high] * pollution [no pollution, linoleum]*

Name	Fixed effect	Std. Error	p-value
(Intercept)	0.273	0.030	0.000
Material AM	0.032	0.034	0.355
Load medium	0.059	0.034	0.085
Load high	0.190	0.034	0.000
Pollution Li	0.214	0.034	0.000
Material AM : Load medium	0.021	0.048	0.657
Material AM : Load high	-0.018	0.048	0.716
Material AM : Pollution Linoleum	-0.008	0.048	0.868
Load medium : Pollution Linoleum	-0.109	0.048	0.025
Load high : Pollution Linoleum	-0.405	0.048	0.000
Material AM : Load medium : Pollution Linoleum	0.009	0.068	0.894
Material AM : Load high : Pollution Linoleum	0.093	0.068	0.171

Table 2 *Summary of the fixed effects from the LME model with the following model syntax (Pinheiro et al., 2017):**odour intensity ~ material [CM, AM] * load [low, high] * pollution [no pollution, carpet]*

Name	Fixed effect	Std. Error	p-value
(Intercept)	0.273	0.029	0.000
Material AM	0.032	0.033	0.336
Load high	0.190	0.033	0.000
Pollution Carpet	0.082	0.033	0.013
Material AM : Load high	-0.018	0.046	0.705
Material AM : Pollution Carpet	0.078	0.046	0.094
Load high : Pollution Ca	-0.188	0.046	0.000
Material AM : Load high : Pollution Carpet	0.045	0.065	0.496

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Supplementary material SM3 – Table

Table 3 Concentrations of compounds emitted from the cement-based mortar (CM), cement-ash-based mortar (AM), linoleum (Li), carpet (Ca) and their mixtures; the results are from the 4 L samples and the concentrations are toluene equivalents in $\mu\text{g}/\text{m}^3$.

Materials	Concentration range [$\mu\text{g}/\text{m}^3$] (4-litre sampling)								
	CM 2.8 m ²	AM 2.8 m ²	Linoleum	CM 1.4 m ² + Li	CM 2.8 m ² + Li	AM 2.8 m ² + Li	Carpet	CM 2.8 m ² + Ca	AM 2.8 m ² + Ca
ALCOHOLS									
1-Dodecanol							1		
1-Ethoxy-2-propanol									
2-Ethyl-1-hexanol							1		
Benzyl alcohol		1					4		
n-Butanol	3	2	6	7	3	3	6	3	4
Phenol	1						1		
Triethylene glycol	220	10					3		6
Trimethylsilanol	<1						1		
Sum Alcohols	224	13	6	7	3	3	17	3	10
ALDEHYDES									
Benzaldehyde	2	2	1	2	2	2	5	1	2
trans-2-Decenal									
Dodecanal							2		
Pentanal									
n-Decanal	3	2	2	3	2	2	3	2	1
n-Hexanal	2	1					2		
n-Nonanal	4	4	6	5	3	3	6	3	3
Octanal		1	2		1		2		
Sum Aldehydes	11	10	11	10	8	7	20	6	6
ORGANIC ACIDS									
Acetic acid	16	7	33	13	14	12	69	13	26
Butanoic acid			7		1				
Decanoic acid (Nonanoic acid)	2		2	1	2		2		
Formic acid			45	8		15			15
Heptanoic acid			9		2				
Hexanoic acid	1		28	3	6	4	3		1
Isobutyric acid			2						

Lactic acid						2		1	2	
Nonanoic acid			5		2			1		
Octanoic acid			13		4	1		1		
Pentanoic acid			9							
Propanoic acid			33		4					
Sum organic acids	19	7	186	25	35	34		76	14	44

ALKANES

2-Methylpentane (3-Methylpentane) (Isohexane)										
Methylcyclopentane										
Cyclohexane										
C6 (Hexane)										
C15 (Pentadecane)	3	4			4	2	3		2	2
C16 (Hexadecane)	2	3			3	2	2	2	2	3
Hexamethylcyclotrisiloxane	2	2	1	2			2	1		1
Sum alkanes	7	9	1	9	4	7		3	4	6
Sum other iso/cyclo-alkanes:	100	135	4	115	83	86		11	65	100

OTHER COMPOUNDS

Acetone	3	3				3		3	2	
N-Methyl-2-pyrrolidone			1							
gamma-Nonalactone			2							
n-Butyl acetate	2							1		
Benzothiazole								1		
Dicarboxylic acid ester			2					2		
Dibutyl eter			1	2				1		
Toluene	1							1		1
Sum other terpenes:			1					1		
Sum VVOC (< C6):	4	4	45	8	4	15		4	2	15
TVOC (C6-C16):	364	174	169	160	132	122		134	92	152
Sum SVOC (> C16):	<1	<1	<1	<1	<1	<1		<1	<1	<1
TVOC <small>Toluene equivalents (ISO 16000-6):</small>	141	65	<1	69	14	3		43	<1	48

Supplementary material SM1 – Figures

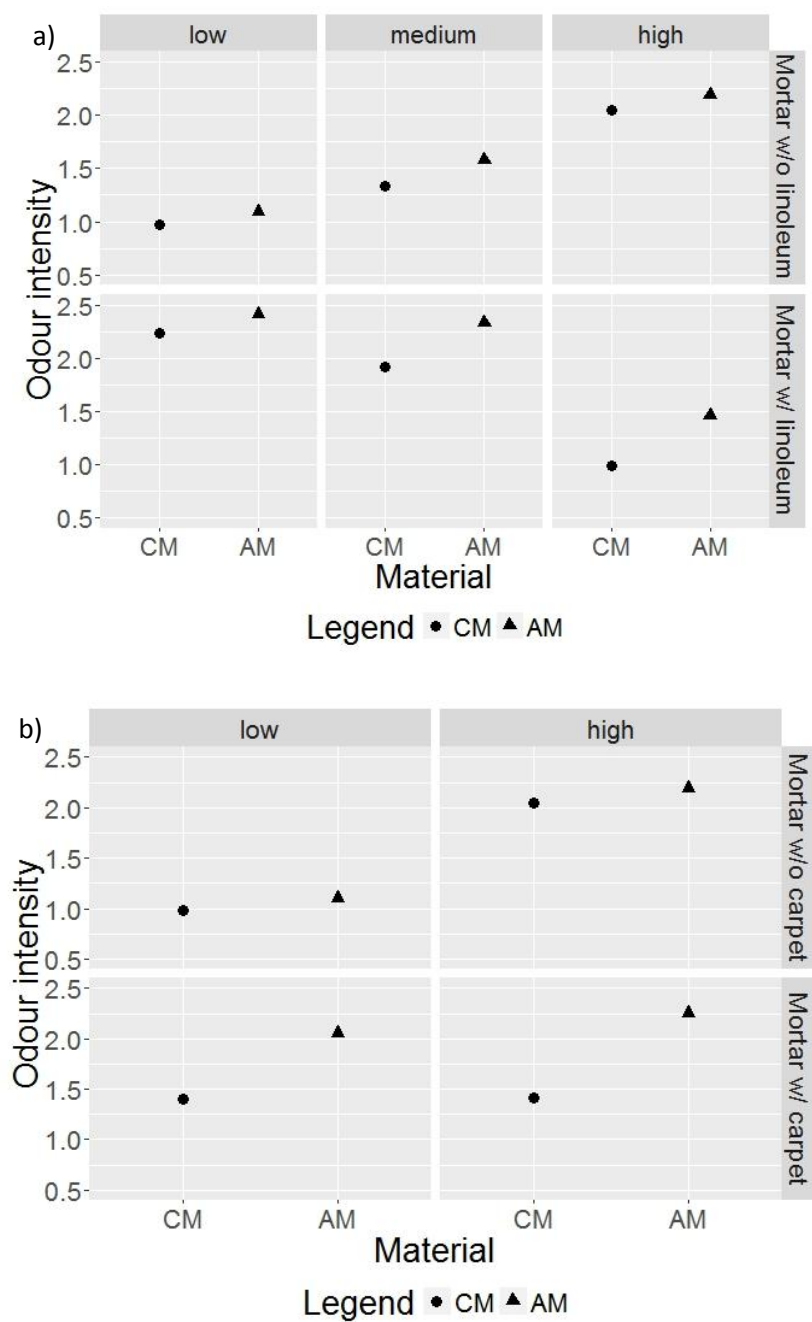


Figure 1 Mean odour intensity of different levels of CM and AM samples singly and together with samples of (a) linoleum or (b) carpet; low loading corresponds to 1.4 m², medium to 1.9 m² and high to 2.8 m²

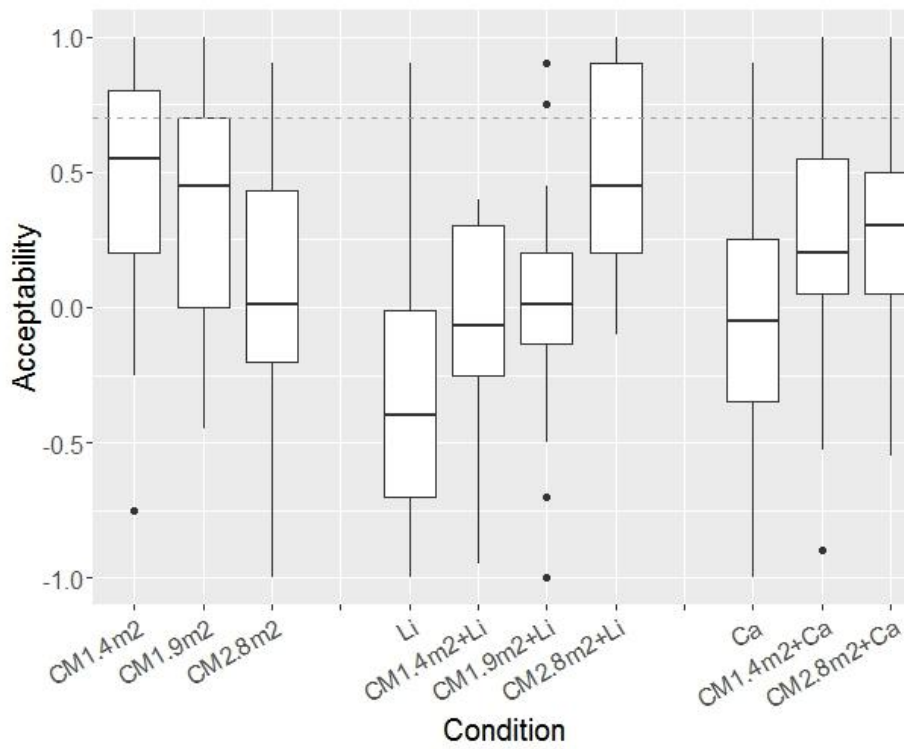


Figure 2

Acceptability of quality of air polluted by cement-based (CM) mortar slabs, linoleum, carpet and their combinations; CM – cement-based mortar, Li – linoleum, Ca – carpet, dashed line reports median of acceptability of air quality of the empty glass chamber (ACC = 0.7)

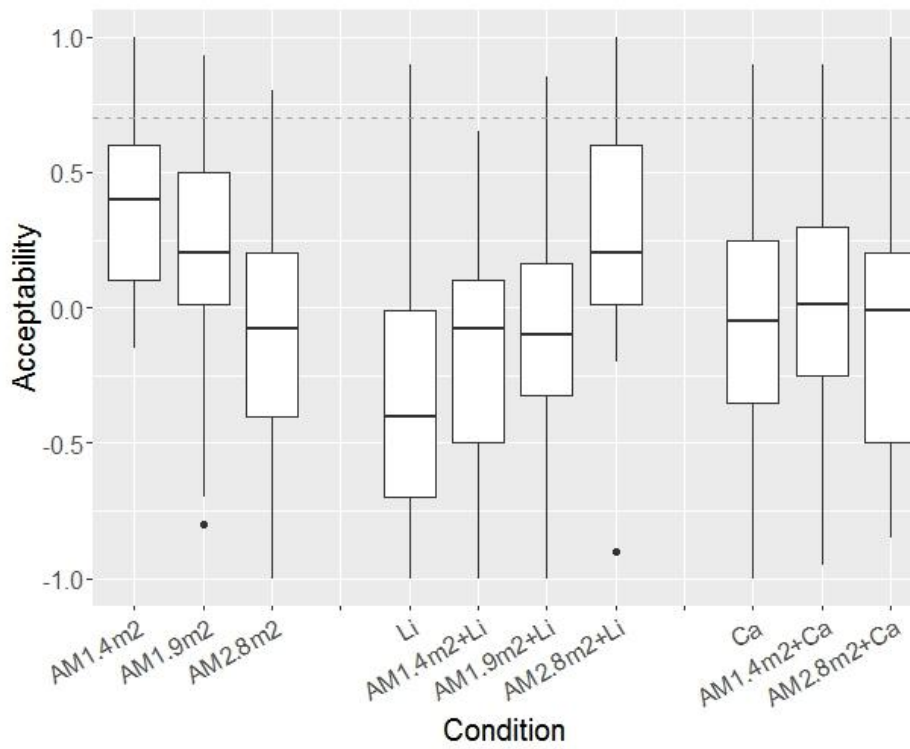


Figure 3

Acceptability of quality of air polluted by cement-ash-based (AM) mortar slabs, linoleum, carpet and their combinations; CM – cement-based mortar, Li – linoleum, Ca – carpet, dashed line reports median of acceptability of air quality of the empty glass chamber (ACC = 0.7)

Supplementary material SM2 – Figures

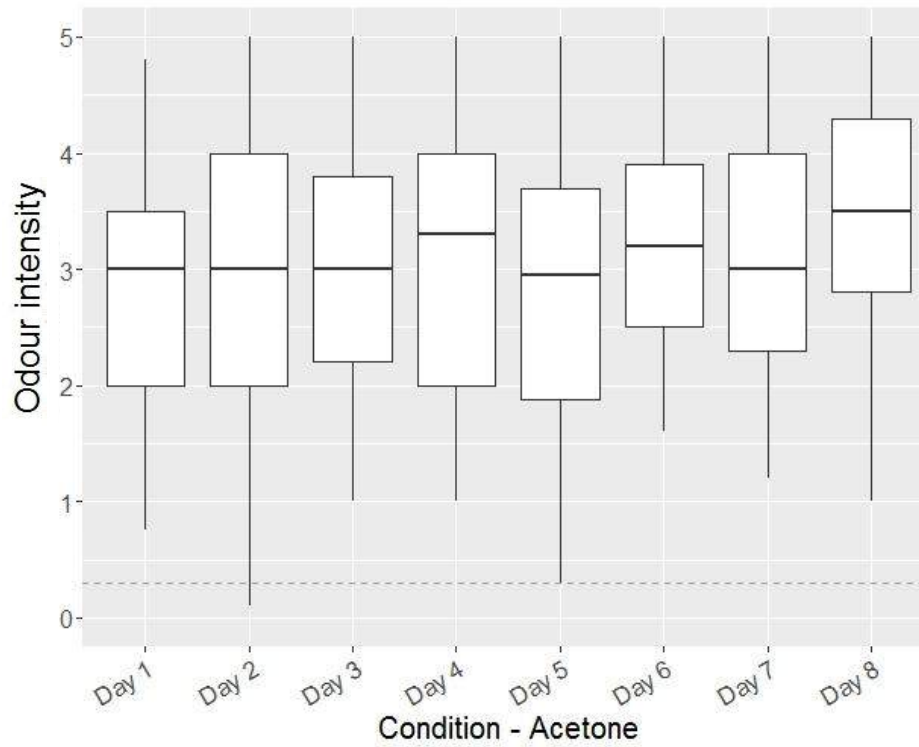


Figure 4 *Boxplots presenting assessment of odour intensity of air polluted by 2-Propanone (Acetone), dashed line reports median of odour intensity of the empty glass chamber (OI = 0.3).*

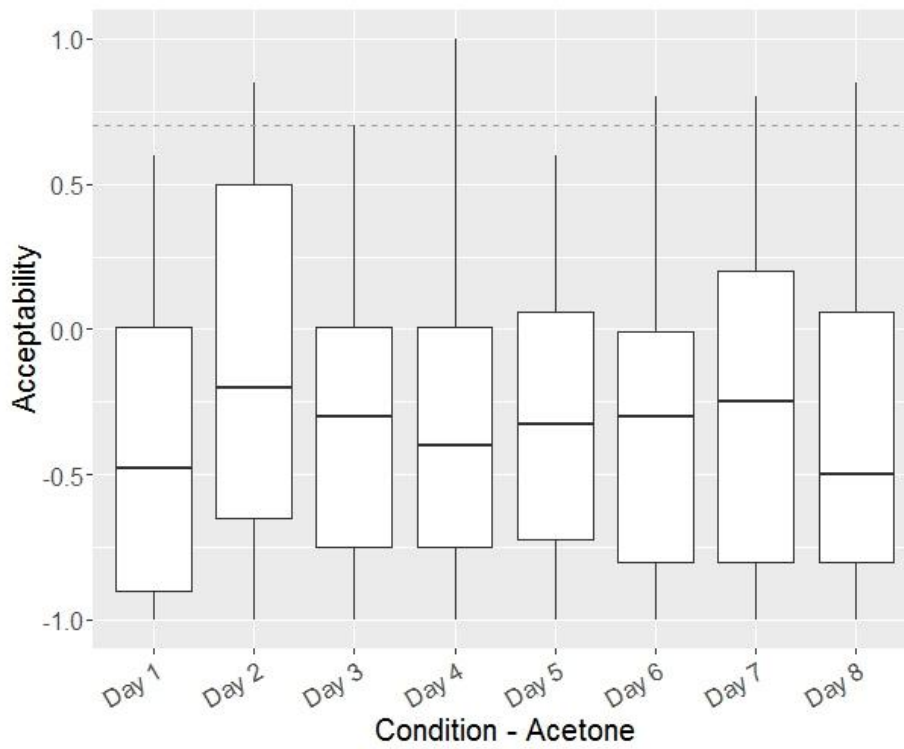


Figure 5 *Boxplots presenting acceptability of quality of air polluted by 2-Propanone (Acetone), dashed line reports median of acceptability of air quality of the empty glass chamber (ACC = 0.7).*

Supplementary material SM4 – Figure

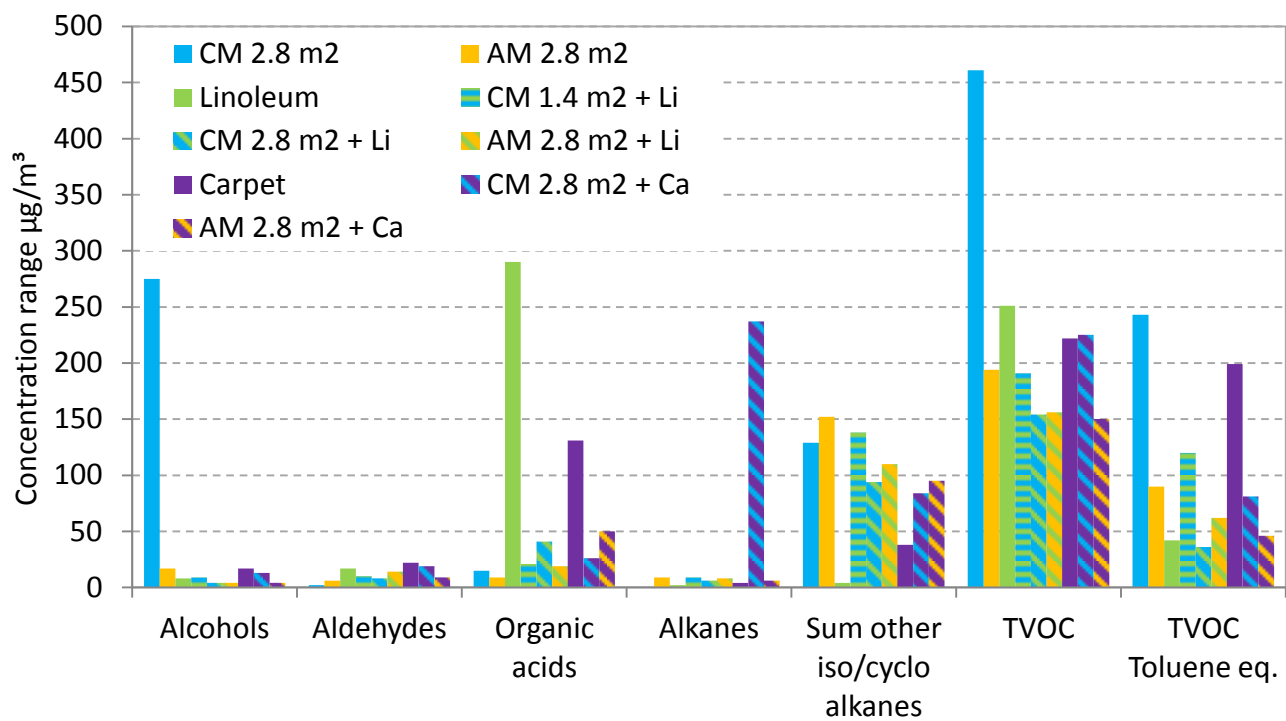


Figure 6 *Concentration ($\mu\text{g}/\text{m}^3$) levels of different compound groups under different material loadings and concentrations.*