Cracow University of Technology

Chair of Building Materials Engineering
Faculty of Civil Engineering

Review Report on the PhD thesis submitted to the
Faculté des Sciences appliquées Département ArGEnCo, UNIVERSITY OF LIEGE
Faculty of Civil Engineering, WARSAW UNIVERSITY OF TECHNOLOGY

to attain the
Degree of Doctor of Philosophy (PhD) in engineering science and technology
and tytuł doktora nauk technicznych w dysyplinie inżynieria lądowa i transport

entitled

"Geopolymer composites based on fly Ash from co-combustion of coal and biomass"

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Supervisors
Professor L. Courard
Professor A.Garbacz

In the beginning, I want to congratulate Mr Piotr Prochoń and the thesis Supervisors Profesor Luc Courard and Professor Andrzej Gabacz for the interesting topic of research carried out in the framework of this thesis. I recognise an enormous effort involved in running a multi-threaded experimental research program. I know how much time and effort it takes to carry out this kind of work. The research concerned numerous material aspects and used several experimental tools, including advanced material identification analysis. The candidate has shown great rigour in presenting the results of the work reliably and comprehensively. I hope that my remarks will positively influence the final presentation of results during the defence, fully illustrating the scientific achievement of Mr Piotr Prochoń.

The presented review report is organised in the following sections:
i) project background, ii) a general description of the manuscript, iii) analysis of the work of candidate in the thesis iv) list of queries and v) final evaluation statement.

i) Project background

Alkali activated materials (AAM) and their subgroup geopolymers are considered more ecological alternatives to Portland cement binders. Also, the technological processes related to the production of geopolymers allow the use of solid wastes from the industrial and energy sectors. The numerous researches are available in the literature based on various precursors and activators, showing the great potential of AAM.
In the doctoral dissertation, Mr Piotr Prochoń refers to the issue of the application possibility of fly ashes from coal combustion (RFA), co-combustion of coal with wooden biomass (CFA) and derived from biomass combustion (BFA), and verification of the potential of using them for the production of geopolymer mortars for masonry application.

ii) General description of the manuscript

This PhD thesis consists of 6 main chapters, and it comprises 172 pages. It begins with an introduction to the subject, which presents the background and motivation of the research. The following, Chapter 2, consists of a literature review based on 305 publications. The literature review is based on recent publications and is followed by a summary of outcomes of the literature survey.
The chapter *Materials and Methods* presents tested materials composition, and adopted testing methods for fly ashes characterisation, and also procedures to test fresh and hardened geopolymer mortars properties. The following chapter 4 the research on the effect of alkaline activators on fly ash geopolymer was presented. Chapter 5 describes author investigations on the effect of CaO addition on

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fresh and hardened geopolymer mortars. In chapter 6, the candidate concludes and defines research perspectives. The document also comprises the list of references and annexes with research results.
The thesis is prepared in good editing standard. All the figures are carefully designed and presented in the text. The language is comprehensive and coherent while some errors and inaccuracies are present, but they do not affect the general good impression on the manuscript.

iii) analysis of the work of candidate in the thesis

The work concerns an interesting issue related to the management of high-temperature combustion wastes (biomass and co-combustion fly ashes) for the production of mineral binders, allowing the replacement of classical fly ashes that are considered to be scarce resources. The study aims to develop new rendering and masonry mortars using alkali activation process of fly ashes.

In the literature review presented in chapter 2 (pages. 25 – 59), the overview of information related to fly ashes production, characteristic, and the influence of the used combustion fuel on their properties. In this study, three potential fly ashes were considered: fly ash from coal combustion (RFA), co-combustion fly ash of coal with wooden biomass (CFA) and fly ash derived from biomass combustion (BFA), as the mineral precursors for the production of geopolymer binders. In my opinion, the information presented in this chapter was gathered skilfully. The description of the ashes production process their composition and morphology show their applications potential. In the manuscript, author refers to the recommendations related to fly ashes application in concrete technology that can be found in the standards. Moreover, he also refers to the EN 998-1 and EN 998-2 for rendering and masonry mortars due to the planned applications of the developed mortars. Have you found in the literature any reports on the possibility of using geopolymers as renderings?
State of the art summarises in quite an efficient way the recent advances in geopolymer technology. It should be emphasised that it was undoubtedly a difficult task to prepare a literature review, taking into account the significant number of recent literature sources on the subject.
The outcomes of the literature survey, based on 305 publications are summarised by the author. The author aptly points out that the requirements for geopolymers and AAM they are not described in standards and are not conform to most national and international material standards. The author perceives the issue of the variations of the chemical compound in fly ashes from co-combustion or combustion of biomass that may be the biggest obstacle to the commercialisation of this type of binders. He also notes that the properties of the alkali-activated binders are strongly dependant to controlled nature and chemical composition of the alumina silicate raw material, and the type and concentration of the alkaline activator.

Please explain your statement (page 53): "The geopolymer mortars usually exhibit a high flexural strength and a low compressive strength".

The main aims of the experimental investigation were as follows from 1 to 3 (aims presented – p. 59):

Aim 1. Characterise the fly ashes from different combustion processes

The candidate, in his research, tested and characterised three types of ashes. He evaluated the possibility of their use as precursors for the production of alkali-activated binders. The experimental methods are appropriately selected, and their description is carefully presented. Chapter 3.5 is dedicated to the presentation of the results of fly ashes characterisation tests. In my opinion, those tests were carried out was great care, and the results were presented in a clear manner. Moreover, it should be noted that the scope and diversity of the conducted identification tests significantly expanded the candidate's research competences, enriching his experimental background.

Aim 2. Characterise the influence of different activators on alkali-activated mortars from co-combustion, and biomass combustion fly ashes;

The performed and discussed preliminary tests, enabled the candidate to identify the positive effect of sodium hydroxide and sodium silicate combined activator; determine the effect of phosphorus and calcium oxides. Moreover, he identified the impact of the increase in the molar concentration of NaOH and low alumino-silicate oxides experimentally, confirming the relationships presented in the literature for the investigated precursors.

Why you enumerate quicklime and BFA among the activators (3.6, page 83)? Those are mineral components added to modify the oxide composition of the precursor. "(...) *Mortars activated with sodium hydroxide and quicklime* .....(...)" in my opinion it would be more appropriate to state that: "*in mortars, the composition of precursors was modified with quicklime and activated with sodium hydroxide solution*".

On what basis the mix proportions of the tested materials were selected? The reader has a strong impression that *the trial and error method* in the search for the optimal mix composition was used. Please include in the presentation the premises for choosing these specific compositions and explaining the expected results or trends.

The preliminary research enabled the author to preselect the compositions for further investigations related to the study of the effect of calcium oxide levels. Please explain why you have not considered in the following section the use of activator based on the mix of sodium silicate and sodium hydroxide. In the literature, this type of activator composition is frequently used. The results of the preliminary study were quite promising in term of mechanical performances (RFA-N5-S22 fc=14 MPa). With CaO blending it could lead to positive results...

Aim 3. Assess the mechanical properties and durability of alkali-activated materials with calcium addition in line with standards for plastering/rendering and masonry mortars (IH. preferably calcium oxide than calcium)

In this section, the candidate tested the partial substitution of the precursors mass (by 2%, 5% and 7%) with calcium oxide addition: quicklime (CaO) and a biomass fly ash with a high level of calcium (BFA) investigating fresh and hardened properties of obtained mortars. Mortars were activated with sodium hydroxide, and modified with quicklime (RFA-N5-C5 and CFA-N5-C5) offered the highest mechanical properties and were assigned compliant for M5 mortar requirements: potential use as masonry and rendering/plastering mortars. The developed mortars applications were limited to inner walls and inside works as a result of freeze-thaw cycles. RFA-N5-B5 was classified: general-purpose mortar with lower mechanical properties for non-bearing inner walls and CFA-N5-B5 could be used as a 2.5M mortar for inner walls.
The author achieved his goal, tested and assessed the suitability of the mortar for building applications

After getting acquainted with the work, I believe that a more appropriate dissertation title would be: "*Feasibility study of alkali activation of fly ashes from combustion and co-combustion of coal with biomass for masonry mortars application.*"

iv) list of queries

1) In my opinion, one of the most problematic issues related to the production of AA binders is the lack of design methods. From this perspective, what are the guidelines or indications for designing geopolymers allowing obtaining optimal strength parameters or the desirable properties? What designing method would you recommend? In your opinion, what would

be the chemical and physical requirements for fly ashes selection, essential to get the highest mechanical properties and durability of AAMs?

2) In the state-of-the-art, you do not refer to the efflorescence. This issue is considered a technological obstacle in geopolymer commercialisation. Have you observed any signs of efflorescence on the surface of samples in developed materials? Do you consider efflorescence as a problem in the planned applications of AAMs for plastering/rendering and masonry mortars?
3) You are pointing at the potential of geopolymer application as the sustainable material with a low carbon footprint. The CO_2 emissions may be strongly affected by the calculation methods of and the energetic expenditure related to processing, and transport of raw materials, mix design energy expended during the manufacturing of the alkaline activators and the energy used during elevated temperature curing. Please position your AA materials in this context and rank them concerning the carbon footprint.

v) final evaluation statement

The manuscript prepared by Mr Piotr Prochoń presents an experimental program that contributes to the application of fly ashes type RFA, BFA, CFA in alkali-activated materials technology. Comprehensive experimental program conducted by the candidate and the diversity of the identification tests significantly expanded the candidate's research competences, enriching his research skills.
The author achieved three goals of the doctoral dissertation by examining properties of selected FA, demonstrating the potential of RFA and CA for alkali activation. Moreover, he pointed at the possible use of BFA as a calcium oxide reach mineral addition for AAM modification. The investigations on AA binders based on RFA and CFA has shown their application for general-purpose masonry mortars with lower mechanical properties for non-bearing inner walls.

Without doubt, as the candidate mentioned it in perspectives, further experimental studies would be necessary to understand the alkali activation process fully. Many questions remained unanswered regarding, inter alia, the definition of the rheological model, the adjustment of type of plasticisers that would be effective in highly alkaline mixes.

Mr Piotr Prochoń, the author of the thesis entitled: "Geopolymer composites based on fly Ash from co-combustion of coal and biomass" proved to have an ability to perform research and to achieve results of a scientific value. Moreover, the candidate presented the capacity to implement scientific results in construction practice. Taking into account the above, I do accept the oral defence of this thesis.

Respectfully,

Place: Cracow
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