UNIVERSITÉ LAVAL

Faculté des études supérieures et postdoctorales

REVIEWER'S REPORT ON A *Ph.D.* THESIS

Candidate : **Mr. Piotr PROCHOŃ**

Institution: **University of Liège / Warsaw University of Technology**

Title of the thesis : ***Geopolymer composites based on fly ash from co-combustion of coal and biomass***

Reviewer : Benoit Bissonnette

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Is a digital marked version of the thesis submitted with this report ? [x] Yes [ ] No

I. General comments on the scientific content and value of the thesis

In order to reduce the carbon footprint of the cement industry, increasing efforts have been devoted in recent years towards the development of alternative binders (partial or complete substitution). In this context, alkali-activated aluminosilicate materials (AAM's) show quite interesting potential. The doctoral work of Mr. Piotr PROCHOŃ is devoted to the study of alkali-activated mortars prepared with fly ashes from traditional sources (coal industry), from co-combustion with biomass and from combustion of biomass only, using a range of alkali activators. The use of fly ash generated with biomass (partially or exclusively) as precursors in AAM's is not well documented and understood. The research work presented in the thesis therefore constitutes a contribution that is undoubtedly original and significant.

The thesis is divided into 6 chapters. The organization of the document is logical and does reflect the thought process and progress accomplished through the different steps of the project.

The context of the study, the objectives pursued and the structure of the thesis are presented in the introductory chapter (chapter 1). There are two main experimental phases in the work: 1) a screening program where a range of AAM mixture, prepared with three selected fly ash (from coal combustion – RFA, from co-combustion with biomass – CFA, from biomass combustion – BFA) and seven different activating systems, were subjected to a limited set of characterization tests, including compression and flexural strength tests; 2) based upon the results from the preliminary phase, a second series of AAM's was prepared with RFA and CFA as precursors, a sodium hydroxide activator and different rates of calcium additions, either in the form of free lime or BFA.

An extensive review of the scientific documentation is proposed in chapter 2. It addresses successively the general characteristics and chemical makeup of the different categories of fly ash considered in the study, the general European regulation framework for both rendering and masonry mortars, and finally the chemistry and general physical properties of alkali-activated matrices prepared with fly ash. Overall, the overview carried out reveals excellent knowledge by the candidate of the various topics relevant to the study. Moreover, the remarkable body of references put together is well exploited throughout the document.

The third chapter consists of a general description of the methodological approach implemented in the different phases of the research program conducted by the candidate. The experimental program is ambitious, with a handful of characterization and behavior tests, and strategically designed. The various standardized tests used in the experimental protocol are described adequately. The information is presented in a generally clear and consistent manner, with proper reference to its subsequent use in the different parts of the study.

Chapter 4 is devoted to the first part of the experimental program, which consisted in a preliminary evaluation (*screening* test approach) of alkali-activated mortar mixtures prepared with the three studied fly ashes (RFA, CFA, BFA) and a selection of activators, four single-component ones (sodium hydroxide or calcium oxide, at two different concentrations) and three others combining two components (from sodium hydroxide, sodium silicate and calcium oxide). Overall, 21 MMA's were subjected to a set of characterization tests and

examinations: mechanical strength testing (compression, flexure) and microanalysis experiments (TGA, FT-IR and SEM). These efforts allowed to characterize the influence of the studied formulation parameters on targeted properties and characteristics of alkali-activated systems in view of their optimization in a subsequent stage. The treatment and analysis of the experimental data are rigorous. In particular, the discussion supported by the infrared spectroscopy data is very interesting and helpful in shedding some light on the complex cross-influence between the different composition parameters and improving our general understanding of the studied AAM systems. The results and conclusions from this preliminary phase formed the basis of the subsequent experimental work, leaving out unfortunately BFA as a precursor and exploring the potential of calcium oxide addition in improving the microstructure and general properties of the investigated AAM's.

In chapter 5, the results of a more comprehensive program focusing on AAM's prepared with the coal combustion (RCA) and co-combustion with biomass (CFA) fly ashes, activated with sodium hydroxide and various amounts of calcium oxide (two sources: free lime, BFA) in replacement, are thus presented and analysed. In addition to the characterization tests and examinations performed in the preliminary program, the experimental strategy was strengthened with the determination of fundamental physical properties (density, porosity, capillarity, water absorption) and durability testing (drying shrinkage, freeze-thaw). The amount of work accomplished is impressive and provides invaluable information towards the optimization and practical exploitation of fly ash-based AAM's. When considering the overall picture, the best results were obtained for RFA-based systems with 5-7% free lime substitution, which seemingly promoted enhanced geopolymerization conditions and a denser microstructure. The alkali-activated mortars prepared with the co-combustion fly ash and the same activators also exhibited mostly satisfactory characteristics and properties with respect to the standard M5 mortar requirements, except for frost resistance. Although the short-term (28-day) requirement was satisfied, it must also be pointed out that the CFA-based mortars exhibited twice as much long-term shrinkage as the RFA. The various microstructural characterization results generated in the program are judiciously exploited by the candidate to explain these differences in durability performance. Still, the results demonstrate in a convincing manner the possibility of designing alkali-activated mortars meeting standard requirements with both RFA and CFA, for different ranges of applications.

In the conclusion chapter (chapter 6), a brief overview of the results and trends obtained in the different parts of the research program is first presented. Overall, the proposed summary reflects adequately the outcome of the research work. In the second section, guidance for future research on the subject is provided through a series of well-advised, useful recommendations.

II. Specific comments and questions on the thesis

The presentation of the research plan in chapter 3 would benefit from a more explicit and detailed description of the experimental variables of the program with regard to the materials studied and some fundamental related information.

- The flowchart (Fig. 23) giving an overview of all steps of the experimental program is comprehensive. Nevertheless, it would be desirable to present in a summary table all variables in the test program, i.e. the different constituents used (investigated precursors and activators) and the various tested combinations.
- It also seems important to substantiate the choices that were made regarding these variables, notably the tested combinations and rates of addition (in chapter 3 or in the two subsequent chapters of the document, where it is most relevant).
- In the development of the research program, was it considered / attempted to use biomass combustion fly ash and co-combustion fly ash from the same biomass source, in order to improve our understanding of the complex interacting influence between the fuel sources upon the resulting fly ash composition and characteristics?

Additional explanations on the mortar mixture design presented in both experimental phases (chapters 4 and 5) would be useful. In particular, the following aspects should be given consideration:

- What were the guiding mixture design parameters (mass ratios between the various solid constituents, water to solid ratio, added water vs. water from the added solution, etc.)?
- Were there any admixture (plasticizing, air-entraining, etc.) used?
- Air content (plastic state) and frost resistance were assessed, but without any disclosed means for air entrainment. Was only naturally entrapped air counted on for frost resistance and were air-void characteristics other than the volume evaluated? In such case, could this be a factor in the observed performances?

The decision for leaving out BFA as a precursor material at the end of the preliminary phase should be explained in more details and substantiated. The results obtained with the N5-C10 and N5-S22 activator combinations actually met the M5 strength requirements referred to in the subsequent chapter. Hence, the question comes naturally: why was it not given a shot in the subsequent phase?

In chapter 5, the drying shrinkage experiments revealed quite significant long-term shrinkage deformations underwent by the investigated alkali-reactive mortars, of the order of 2000 μm/m (RFA-based systems) to 4000-5000 μm/m (CFA-based systems), depending on the type of precursor being considered. Are not such high shrinkage values linked with the state of cracking observed in some cases in SEM examinations, not only in phase 2 of the experimental program, but in the first phase (preliminary) as well? Recent studies (e.g. Rodrigue *et al.*, 2020) have highlighted this potentially very important issue in AAM's. A more detailed discussion in that regard would have been interesting and useful.

In the conclusion chapter, a rather detailed appraisal of the practical applications where the best performing RFA-based and CFA-based mortars of the study could be used is proposed (Table 32). What were the criteria to develop such a detailed classification and is there enough data available at this stage to back it up with confidence?

Additional comments:

Other comments can be found in the digital marked copy of the document attached to this report.

III. Evaluation and recommendation

The thesis prepared by Mr. Piotr PROCHOŃ is very good. The results obtained and the reflection they have given rise to constitute a significant contribution towards the implementation of alkali-activated materials in the framework of sustainable construction practice.

In my opinion, the candidate has clearly demonstrated the scientific maturity to conduct successfully high-level research on his own.

In view of the above, I consider that Mr. PROCHOŃ should be allowed to defend his thesis.

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