Title: **Geopolymers incorporating wastes and composites processing**

Author of doctoral thesis: Ing. Gianmarco Taveri

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1. Introduction

Presented dissertation of Ing. Gianmarco Taveri deals with the preparation BSG / FA based geopolymer from waste materials. The aim is to use two types of waste material, fluid fly ash (FA) and borosilicate glass (BSG) for the preparation of geopolymer solids and subsequent physical, chemical and mechanical characterization of geopolymer composites of different composition.

In the introduction the author summarizes the reasons for the use of geopolymers, especially ecological ones. It also describes in detail the development of alkali-activated materials from 1930 to the present. He clearly summarizes the limits alkali activated materials and introduces the reasons why these materials are not yet commercially produced. The stability of these materials is discussed from the point of view of alkali-silica reaction, resistance to acid attack, to high temperature, to fire, to freeze-thaw and efflorescence.

The work sensitively introduces differences in terminology and nomenclature in the field of alkali activated materials and geopolymers and describes various scientific approaches to explain the mechanism of formation of these materials. The role of the amount and type of alkaline activator, the ratio of the individual components and the influence of the curing conditions is mentioned. In the thesis there is an overview of the recycled glass and fly ash utilization in geopolymerization and on geopolymer-matrix composites prepared with different types of fibers. At the end of the introduction, the author summarizes past applications of alkaline activated materials and geopolymers and offers potential applications of the future.

Scopes and aims of thesis are clearly and precisely defined.

In the Methodology section of the dissertation, the raw materials used, the geopolymer samples and the cellulose fiber-reinforced geopolymeric manufacturing and hydro pressure sintering (HyPS) process are described. To characterize input materials and final products, the author uses all available methods, which he combines appropriately.

The results have shown that BSG can be used for the preparation of geopolymer materials as substitution of commonly used waterglass and the formation of geopolymer structures has been demonstrated by infrared spectroscopy and nuclear magnetic resonance.

I considered important that the author proved by using ^{11}B NMR that boron is directly involved in the geopolymer structure. In the preparation of geopolymer composites with dispersed cellulose fiber, a significant positive effect on flexural strength and fracture toughness has been demonstrated, especially for the composites with 2 wt. % content of fibers. Furthermore, superficial modification of cellulose fiber by geopolymer matrix and formation of intermediate layer was demonstrated by SEM analysis. It has been shown that the HyPS can also be used in the preparation of geopolymer materials and, when used, increases the crystalline phase content.

The conclusion briefly summarizes the results presented logically based on experiments and analyzes.

Literature list is thorough and includes old and new scientific work dealing with the topic. The appendices suitably complement the presented topic and results.

2. Contribution to the knowledge

Doctoral dissertation presents current and comprehensive look at the issue of alkali activation of materials, especially on the use of waste materials in the preparation of geopolymer based on fluidized fly ash type F and borosilicate glass.

In his work, the PhD student contributed to increasing the state of knowledge in this field by his comprehensive scientific approach. He was able to use borosilicate glass to prepare geopolymer materials in an innovative way and to demonstrate the direct involvement of boron in the geopolymer structure. These results offer new possibilities for the use of various waste materials by alkali activation method.

Furthermore, the author has designed and successfully tested a new method for preparation of geopolymer using hydro pressure sintering, which is currently the subject of patent procedure. This method allows a significant reduction in molarity of the sodium hydroxide used for the geopolymer synthesis.

3. Questions and comments

Objective viewpoint:

Introduction

I don't think glass is 100% recyclable (page 6). There are types of non-recyclable and hardly recyclable glass, such as TV screens glass, car glass, mirrors, and others.

I disagree with your statement on page 8 that geopolymers (GPs) and alkali-activated materials (AAMs) are eligible to 100% replace ordinary Portland cement (OPC) in its applications. Each material has its limits and specific properties and state that these materials are a substitute for cement are misleading. At least until the standards for this kind of materials will be created. This is also related to the topic "Obstacles in the Commercialization of AMMs and GPs", where due to the different chemistry of OPC and AAMs and GPs, the OPC standards used are not always satisfactory.

I'm not sure about the last sentence in the first paragraph of Chapter 2.4.1.: "When concrete is used as a binder, then the word "mortars" is usually adopted [56]". Haven't you meant "When cement…." because: Cement is a fine binding powder that is never used alone, but is a component of both concrete and mortar. Mortar is composed of cement, fine sands and lime; it is used a binding material when building with brick, block, and stone. Concrete is a very strong structural building material composed of cement, sand, and larger aggregate (gravel). Furthermore, I am not sure of the accuracy of the cited reference because this article does not address the issues mentioned in this paragraph.

Scopes and aims

You're declaring that "Therefore, the main aim of this work is to develop and produce an eco-friendly material, with no greenhouse emission, worth of replacing the Portland cement in building and infrastructural and structural applications, while conferring to the material high strength and fracture resistance by dispersing cellulose and waste paper fibres in the matrix.” but waste paper fibers weren’t used in this work. Can you explain the discrepancy?

Methodology

If I well understood, all fly ash was heat treated at 800 °C prior to characterization and alkaline activation to burn all organic matter out. However, type and amount of organic impurities is not presented in charter 5.1. Does the amount of organic impurities correspond to the L.O.I. in table 4? If so, do you really think that 0.7 % is so serious that the ash has to be burned? This is also contradicted by the intentions mentioned in Chapter 3 - development and production of an eco-friendly material with no greenhouse emission. Furthermore, there is no standard according to which the loss on ignition was determined and the reason why this particular standard was chosen. Thermal analysis (DTA/TGA) should be used to identify the amount of organic matter and the temperature of their removing.

I would like to know the temperature at which coal is burned in the Počerady power plant (approximately). According to the chemical and mineralogical composition it is clear that it is a classical combustion and not fluidized bed combustion, but it should be mentioned in the dissertation.

Why have you chosen borosilicate glass that can be recycled?

In Chapter 4.1.2. I wonder why the temperature of 85 °C and the soaking time 1-3 days was selected. Lower or room temperatures are used in the literature. I can’t imagine the use of these curing conditions for the future practical use of this type of geopolymer. On the schemes describing the methodology for preparation of geopolymer samples and composites (Figures 26 and 27) intermediate step of material compaction is lacking. Has any method of compaction been used - if not, why? This step can significantly reduce the pore content and thus affect the resulting mechanical properties.

In the field of mechanical properties I am surprised by the chosen type of test samples. Why these micro samples were chosen instead of 4 x 4 x 16 cm test specimens. If used, the results could be better compared with literature, whether with geopolymer or conventional concrete materials. In addition, microcracks may be formed during cutting of the samples, which may negatively affect the final strength.

Results and Discussion

I consider it a serious mistake that the compressive strengths were determined only for Mix-1 and Mix-2. It is not determined how old samples were, so that results cannot be compared with literature. I miss the results of the mechanical properties of reference samples of the same size prepared from cement / concrete or pure FA-based geopolymer. The mechanical properties have not been observed in the long term period (at least 90 days), as is usual, and therefore it is not possible to confirm that there is no degradation of the structure and loss of mechanical properties of the BSG / FA based geopolymer. How can you claim that these materials can also be used as construction materials when you have no idea of long-term stability?

Why Mix-1 was used for preparation of cellulose fiber-based geopolymer composites when Mix-2 had the best mechanical properties as shown on pages 94 and 95. As part of a comprehensive dissertation I would expect that composites should be prepared for all presented mix designs. Why were the experimental work and especially the mix designs and samples so limited? If you want to stay in science, you will have to significantly improve your attitude towards experimental work.

XRD results have shown higher content of mullite, α-quartz and sillimanite contained in fly ash (21.5 wt. %, 14.9 wt. %, 18.5 wt. % respectively) compared to geopolymer samples (for Mix-1: 5.6 wt. %, 3.1 wt. %, 0.1 wt. % respectively). How can you explain this decrease, e.g. for mullite, with regard to the fact that it is a very stable crystalline phase whose dissolution is described especially at high temperatures (Sammadar et al. https://doi.org/10.1111/j.1151-2916.1964.tb14405.x; Ribeiro et al. https://doi.org/10.1016/j.jeurceramsoc.2004.03.028)?

The discussion is very brief. I would expect it to be more detailed as it is a dissertation.

Page 107: This is the first time when the foaming of geopolymer is mentioned. Theory in paragraph 2 should be moved to the introduction.

Why do you consider source materials to be inhomogeneous (Chapter 6.2.3.)? This statement is not supported by any long-term monitoring of fly ash or BSG parameters.

As one of the results of the dissertation, I would expect a geopolymer structure design that would indicate the involvement of boron directly in the geopolymer network.

Formal viewpoint:

These errors do not affect the scientific content of the dissertation, but significantly reduce its overall quality and readability:
The sizes and types of some graphs are improperly selected. Some data can be very poorly read from the images (Figures 45-46); while some of the graph size is enormous (Figures 3 and 43).
The authors should be cited in the text in a uniform way - some with the initials of the first name, some without. Images and tables are often improperly placed in the text.
Nomenclature should be unified, e.g. geopolymer x geopolymeric, water glass x waterglass.
Page 5, 4 lines above the picture: I assume that the beginning of the last century was meant.
Page 18, title of chapter 2.3.5.: There is a missing letter in a title and there is „freeze-taw“ instead of „freeze-thaw“.
Page 19, the end of first paragraph: It should be noted again the reference number (Brooks et al. [50]).
Page 34, line over the picture: Cation charge is not listed in the index.
Page 41, second paragraph: There is a superfluous gap behind „chemical reduction of iron oxide“.
Page 45: $Ca(OH)_2$ is not shown in italics.
Page 46: There is no space before the parenthesis in the middle of the second paragraph.
Page 75, Table 5: It should be specified in Figure caption which type of density, mentioned in chapter 4.3.1 is presented.
Page 91, first paragraph: Sealing methods were exposed in Chapter 4.1.2.
Page 119, Figure caption: Figure S1b designation is incorrect (right A1b).

4. Conclusion

I consider the search section very good and carefully elaborated. The problem is in the experimental part, both with an amount of experiments and with the presentation and discussion of the results - it seems to me a little inadequate for a dissertation. It is necessary to consider what is for future scientific work more important - the innovative approach of the student or the number of experiments? I believe that a personal approach to experimental work, evaluation of results and their discussion can be improved by our own efforts. But if a person does not have innovative thinking, then the work will only be mechanical and the results will lack a novelty. For these reasons, my conclusion is:

Doctoral thesis made by Ing. Gianmarco Taveri is scientifically good, contains not only a summary of existing knowledge, but also a methodological approach to his own experimental work. The work brings new information about novel type of geopolymer material based on fluid fly ash and borosilicate glass and original method of hydro-pressure sintering which allows a significant reduction in molarity of the sodium hydroxide used for the geopolymer synthesis. I can confirm that the objectives of the work have been met. The author also has sufficient publishing activity (4 articles in foreign impacted journals) and 1 patent proposal was submitted based on his scientific work.

Despite the above mentioned comments I recommend the work of Ing. Gianmarco Taveri for an oral defense.

V Praze, dne 17.7.2019

Ing. Ivana Perná, Ph.D.