Silesian
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PhD Thesis

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Analysis of material properties of industrial waste-based geopolymers for assessment of their usability in construction

Doctoral dissertation submitted in the course of proceedings for the granting of the PhD degree in the discipline of civil engineering, geodesy, and transport

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SUMMARY

CHAPTER 1 INTRODUCTION

The chapter contains the description of background and motivation for the work together with the definition of the problem – the escalating environmental problems, mainly with CO_2 emission and water sources. Geopolymer (the mixture of aluminosilicate material called a precursor and liquid activator) is considered as an environmentally friendly alternative for ordinary Portland cement concrete which production consumes significant amounts of water and is responsible for significant CO_2 emission. Despite savings on CO_2 emission and extent water consumption, geopolymer allows to reuse many kinds of industrial waste (including the hazardous one) inside its matrix. The use the various kinds of waste as the precursor is popular, but the aggregate role is still the most often played by natural materials such as sand. This Thesis respond for that issue offering solution in the form of discarded, crushed CRT glass aggregate. The reuse of CRT glass inside geopolymer in form of an aggregate offers simultaneously the solution of the problem of safe recycling of that hazardous waste
The chapter presents as well four research hypotheses:

Hypothesis 1: Discarded CRT glass can be used in metakaolin-based geopolymer in the role of aggregate without special pre-treatment.
Hypothesis 2: Metakaolin-based geopolymer with CRT glass can be considered as a building material, regarding to the flexural and compressive strength
Hypothesis 3: Metakaolin-based geopolymer with CRT glass can be cured in different temperatures without crucial impact on strength.
Hypothesis 4: The incorporation of CRT glass inside metakaolin-based geopolymer reduces the danger of environment pollution with heavy metals.

The chapter emphasis also the main aim of this thesis – the presentation and description of the metakaolin-based geopolymer with CRT glass as potential building material together with proposition of the new way of CRT glass recycling – and the minor goals such as: the summary of existing knowledge about the raised topic, the description of the influence of various factors on mechanical behavior of geopolymer, the determination of porosity, density and leaching of heavy metals, the comparison of achieved results with results presented in scientific literature, the summary, conclusions and determination of future goals.

Finally, the chapter shows the organization of this Thesis and characterizes briefly each of eight main chapters.

CHAPTER 2 STATE-OF-THE-ART

The chapter begins with the description of general characteristics of geopolymer with the special emphasis on the chemical characteristics. Geopolymerization is concluded as the process built of three main stages: deconstruction, polymerization and stabilization. Further, the most popular types of precursors are listed and described (metakaolin, fly ash and ground granulated blast furnace slag) but the rarely used are mentioned as well. As the most popular activators there are indicated sodium silicate and sodium hydroxide or potassium hydroxide. Then, the most popular methods of mixture designing are presented. Most of scientists adjusts components of the mixture to obtain the desired Si/Al ratio and Na/Al ratio.

The chapter introduces as well the historical background, starting from the potential ancient beginnings (Jospeh Davidots should be mentioned here as the father of those ideas), through the first published researches (as the most notable scientists should be listed here Hans Kuhl, Arthur Oscar Purdon and years later – Victor Glukhovsky) finishing on undeniable Polish input of

professor Jan Małolepszy, Jan Deja and Wiesława Nocuń-Wczelik. The next part focuses on the more current works carried on all-over the World: in Great Britain, Australia, China, Spain, Portugal, France and United States. The special emphasize has been put on researches done by Jannie van Deventer and John Provis. Finally, the works currently carried on in Poland have been described, focusing mainly on researches published by scientists from Cracow University of Technology and Silesian University of Technology: professor Janusz Mikuła, professor Izabela Hager, professor Jan Kubica, professor Marcin Górski and works published by the Author of this Thesis.

Further, the various possible applications of geopolymers have been described. The civil engineering branch includes the masonry units, pavements, culverts, roof tiles and even the airport runways. Due to the high fire and chemical resistance as well as anti-corrosion properties, geopolymers found application as protective layers for reinforced concrete and steel. The less popular applications include: self-healing materials, 3D printing, restoration of monuments or even the possible material for lunar structures.

The next part is devoted to the CRT glass – the general characteristics, the parts of cathode ray tube, the heavy metals content, the recycling methods (in open loop and closed-loop) and methods of special treating to make it safer for environment. The application of CRT glass in concrete is described precisely, mainly in the role of an aggregate. According to the scientists, application of CRT glass into the concrete structures can be safe way of its utilization but it causes the decrease of strength.

The chapter includes as well the examples of successful immobilization of heavy metals inside geopolymer mixture. Then, the extended presentation of publications devoted to the utilization of CRT glass inside geopolymer mixture is given. The CRT glass has been utilized in geopolymers based on different type of precursors (metakaolin, fly ash, slag and combinations of listed ones) both in a form of a powder and in form of an aggregate.

The chapter is concluded with summary of all information and with the deficiencies both in existing knowledge and researches about geopolymers with CRT glass. As the main deficiency there is defined the lack of the extended research on one type of geopolymer. As an answer to the defined deficiencies, an Author decided to do the extended research on metakaolin-based geopolymer with CRT glass in form of an aggregate. The research includes among the others both flexural and compressive strength tests, the finding of an optimal mixture and study of an influence of various factors on its mechanical behavior.

CHAPTER 3 PRELIMINARY RESEARCH

At the very beginning the graphical scheme of the research part is presented.

Then, the chapter continuous with the characteristics and origin of all materials used during the tests: metakaolin, CRT glass, sodium silicate and sodium hydroxide. Next, the research methods are presented including shape of the samples, description of equipment and used standards. Then, the Author presents the initial tests. The first test has been done on samples containing CRT glass coming from different batches to check the convergence of results. The next test contains comparison between strength of geopolymer containing sand and CRT glass to asses superficially how does the replacement of aggregate influence the mechanical behavior (it occurs that the strength of geopolymer containing CRT glass is smaller than strength of geopolymer with sand).

The next part describes precisely the influence of the CRT glass content on flexural and compressive strength of samples. The whole procedure of the test together with presentation of results and analysis is presented. The flexural to compressive strength ratio and the density has been calculated as well. According to results, there is no monotonic dependence between CRT glass content and mechanical behavior. The range of flexural strength values was equal to

3,6 - 6,2 MPa, while the range of compressive strength results was equal to 41,6 – 50,1 MPa. Fours mixtures have been chosen for the further tests.

The next test has been devoted to the influence of curing temperature on the mechanical behavior of geopolymer. Samples were cured at 20°C, 40°C and 60°C. According to the results, the flexural strength increases along with the increase of the curing temperature while the compressive strength behaves in not monotonic way and is approximately similar for all curing temperatures. Two mixtures and one curing conditions were chosen for the further test.

The last from the initial tests has been focused on the temperature changes inside the geopolymer and the changes of strength over time. Samples were cured at 40°C for the first 24 hours and then at the room temperature. According to the results, the temperature inside geopolymer grows along with the increase of the metakaolin content. The strength of geopolymer samples containing more CRT glass showed the tendency to decrease in time. On the grounds of achieved results, one mixture containing metakaolin to CRT glass in mass ratio 1:1 has been chosen for the main research.

CHAPTER 4 MAIN RESEARCH

The whole main research has been performed on samples containing metakaolin to CRT glass in mass ratio 1:1. All tests are described precisely (samples preparation, curing regime, testing procedure, pictures of samples before and after tests, all results gathered and presented in form of charts, the description and analysis of results).

The first part of the main research describes comparison of the changes of strength over time of geopolymer cured in two conditions: all the time at the room temperature (~20°C), and for the first 24 hours in climatic chamber at 40°C and then at the room temperature. According to the results, curing at elevated temperature assures the rapid growth of strength while geopolymer cured at the room temperature gains the strength slowly. However, after 14 days, the compressive strength of samples cured at the room temperature overgrowth the strength of samples cured at elevated temperature. That difference increased in time. After the test, an Author decided to continue the research on samples cured all the time at the room temperature.

Then, the influence of sodium hydroxide concentration on mechanical behavior has been checked. According to the results, the strength of geopolymer increases along with the increase of NaOH concentration from 6 mol/L to 12 mol/L. It has been concluded that 10 mol/L is an optimal concentration for this type of geopolymer.

The next test describes the influence of CRT glass particle seizes on mechanical behavior. No evident dependence between CRT glass particles size and flexural nor compressive strength values was observed. In further tests, the CRT glass of particles size in range (0 mm: 4 mm> has been used.

At the end of the main research part, an Author investigated the behavior of the geopolymer made of the chosen mixture over long period of time (1 day – 112 days). Generally, both flexural and compressive strength increased in time. No monotonic dependence between flexural strength to compressive strength ratio (fx/fc) has been noticed. That part of the chapter includes the comparison of dependence between flexural and compressive strength of metakaolin based geopolymer with CRT glass and flexural to compressive strength dependence presented by different codes and standards as well as by other scientists. Summarizing, the tested geopolymer should be considered as the brittle material so the proper reinforcement has to be applied.

CHAPTER 5 COMPLEMENTARY RESEARCH

The complementary research has been done on samples containing metakaolin to CRT glass in mass ratio 1:1 and cured all the time at the room temperature.

The first from the complementary tests describes the porosity of geopolymer. The average total porosity was equal to 13,7% while the average density of geopolymer was equal to 1,80 g/cm^3.

The next test concerned physical and chemical characteristics and has been done with the use of atomic absorption spectrometry. The examination of leachate from geopolymer incorporating CRT glass has been compared with leachate from not-stabilized CRT glass. According to the results, the amount of leached heavy metals (especially Pb) is significantly limited when CRT glass is closed inside the geopolymer matrix. The achieved values were compared with binding standards. The only examined characteristics of leachate from the hardened geopolymer which did not fulfill standard limits was pH.

CHAPTER 6 DISCUSSION

The chapter contains the comparison of results achieved during all tests with findings of other scientists.

Regarding to the influence of various CRT glass content on mechanical behavior, scientists are divergent. Some publications claim the increase of strength along with the increase of CRT glass content and some the opposite dependence. Due to the limited number of publications devoted to CRT glass added to the geopolymer in form of an aggregate, that subsection is presenting also the sources describing geopolymers with CRT glass in form of a powder and concrete with CRT glass aggregate. The majority of cited publications describing concrete with CRT glass aggregate reports the decrease of strength along with the increase of CRT glass content.

Scientists are more aggregable about the influence of curing temperature on geopolymer strength. Most of researchers noted the increase of strength along with the increase of curing temperature, although, some of them reports the optimal value of curing temperature above which, the strength starts falling down. However, there are also sources reporting that geopolymers cured at room temperatures (20°C or even lower) achieve higher (especially long-term) strength than geopolymers cured at elevated temperatures.

Many scientists determined the changes inside the geopolymer mixture with the use of isothermal calorimetry. As in this Thesis, scientists report appearance of exothermic peaks. The first peak occurs while metakaolin particles are dissolving (in dependence on accuracy of measurement, some scientists identify here two peaks) and the second one is caused by the polymerization process.

According to results described in the scientific literature, the strength of geopolymer increases in time. Geopolymers cured at elevated temperature gains the strength more rapid than geopolymer cured at the room temperature. Some sources report that long-term strength of geopolymer cured at the room temperature overgrows the strength of geopolymer cured at the elevated temperature. Those conclusions are convergent with findings withdrawn within this Thesis.

The most of scientists declare that geopolymer strength increases along with the increase of activator concentration, although, many of them do not indicate the highest tested value as an optimal one, mostly because of economic aspects and because of the rapid decrease of workability of a mixture. Despite, some publications report the decrease of strength above the given value of activator concentration.

The quantity of publications devoted to the CRT glass particle size on mechanical behavior is limited and the one found by the Author are presenting divergent conclusions.

The total porosity of metakaolin-based geopolymer with CRT glass is smaller than in most of cited publications. In case of the bulk density, some sources give smaller and some, higher values than the one found within this Thesis.

Most of the cited publications confirms that the concentration of heavy metals in leachate from geopolymer incorporating CRT glass is significantly smaller than in leachate from not-stabilized CRT glass (what is convergent with the result obtained within this Thesis). Some sources declare that geopolymer with CRT glass fulfills regulatory limits and some declare that not or, that its dependent on CRT glass amount.

CHAPTER 7 SUMMARY AND CONCLUSIONS

The chapter begins with the summary of the research part of this Thesis. Then, the chapter presents the following final conclusions drawn on the basis of the research part of this Thesis:

- The CRT glass content does not influence significantly the mechanical behavior of geopolymer.
- Elevated curing temperature provides higher early strength and ability of quicker demolding than curing at the ambient temperature. Although, long-term strength of geopolymer cured at ambient temperature surpass strength of geopolymer cured at elevated temperature.
- The increase of an activator concentration led to the increase of strength and decrease of the mixture workability.
- The change of CRT glass particles does not influence significantly the strength.
- The temperature inside the geopolimer during the curing process increases along with the increase of metakaolin content.
- The concentration of chosen heavy metals in the leachate from geopolymer fulfills the regulatory limits.

Conclusions drawn in the response to the initial hypotheses:

1. CRT glass can be used as an aggregate in metakaolin-based geopolymer without any additional treatment.
2. Metakaolin-based geopolymer with CRT glass has good mechanical characteristics (flexural strength 5-6 MPa, compressive strength 50-60 MPa, density 1850 kg/m^3) and therefore can be potentially considered as building material although, one can be aware of its brittleness.
3. Both geopolymer cured at ambient as well as in elevated temperatures showed good mechanical behavior, although, geopolymer cured at ambient temperature should be demoulded later (7 days was found as enough) to avoid cracks.
4. Addition of CRT glass to metakaolin-based geopolymer helps in immobilization of heavy metals in comparison to not-stabilized CRT glass.

CHAPTER 8 DIRECTIONS FOR FURTHER RESEARCH

The chapter contains the main research directions planned by the Author for the future. The list includes among the others: determination of changes of the geopolymer strength over years; the influence of humidity and freeze and thaw cycles on the mechanical behavior; determination of material's rheology; the influence on the living organisms, human's health and on the reinforcement; big-scale tests and determination of the boundary surface of the material.