University of Pannonia
Chemical Engineering and Material Sciences Doctoral School

Potential uses of alternative raw materials for the production and application of silicate-based inorganic polymers

Ph.D. THESIS

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Introduction and Aim of Research

Today, cement is the most widely used artificial material. However, the cement industry is one of the largest CO_2 emitters and also has a significant landscape destruction effect due to the limestone mining; therefore it is increasingly under attack. There is a growing demand for the development of binders that require different raw material sources and are able to bond and set in a different way than the widely known and used classical hydraulic (cement) binders. Promising solutions could be alkali activated cements (AAC) (or silicate-based inorganic polymers), which cannot replace cements completely, but can offer serious alternatives in some cases.

The competitiveness of AACs lies in the fact that they can be produced using any powdery material (including various polluting industrial wastes and by-products) with sufficient reactive Si, Al and Ca content. In addition, the matrix of AACs can bind other wastes and thus can be an integral part of the circular economy model. The fact is not negligible, that with the production of lightweight/foamed structural elements, individual applications may also appear. As eco-friendly porous materials, AAC foams have considerable potential in environmentally and economically relevant areas (e.g. thermal and acoustic insulation, pH control, air and wastewater treatment) due to their favourable production conditions and promising properties.

The primary goal of the research was to follow the "waste-to-profit" principle, which was to be achieved in two ways. On the one hand, the aim was to convert industrial by-products and waste materials by alkaline activation into higher added-value products whose mechanical properties are competitive with those of traditional binders. On the other hand, the objective was to demonstrate that multifunctional AAC foams with controlled properties can be developed by foaming contaminant-free components, which can be used to reduce air and water pollution and energy loss. By producing AACs based on CaO-poor and CaO-rich raw materials (metakaolin and blast furnace slag) it is possible to find an alternative way to handle the growing global environmental problems and to partially replace the traditional binders.

Experimental

The dissertation is focused on the identification of the problems limiting the practical applicability of alkali-activated cements (AAC) produced and their possible solutions. Based on a review of the relevant literature, it can be concluded that composites produced by the combination of different waste materials show less good mechanical properties than their "classical" binder-based composite counterparts. In addition to the source of aluminosilicate used, the quality of the additive also has a significant influence on the properties of the final product. In the case of combining blast furnace slag with crumb rubber from end-of-life tires, the primary goal was to maximize the strength of the AAC based composites by choosing the optimal crumb rubber/sand ratio, improving the compatibility between the AAC matrix and the rubber particles and using fibre reinforcement. The effects of storage conditions, specimen size and/or shape, and cyclic loading on the compressive strength were investigated, and the resulting figures were compared with the relevant values of classic binders (Portland cement, blast furnace slag cement). Based on the experiments performed, the best result is obtained with the addition of 10 wt% sulphuric acid treated crumb rubber and 1 wt% of kaolin fibre content. The physical properties of such materials are competitive with those of traditional binders.

As eco-friendly porous materials, metakaolin-based AAC foams are not only fire-resistant and chemically inert, but also have a high specific surface area and gas permeability. However, for practical applications, the intense drying shrinkage and crack tendency associated with the extreme water demand of the aluminosilicate source is a major concern. It is essential not only to control the pore size and distribution but also to ensure the optimum strength with high interconnected porosity; the contrast between the latter two features is easily noticeable. In the second part of the experimental work, the foaming process was carried out by the combined technique of saponification/peroxide decomposition/gelcasting (SPG). The effects of H_2O_2 concentration, the type and amount of stabiliser and the addition of slag on physical properties were investigated. The foams were made free of organic matter and cracks through the optimisation of technological parameters (heat treatment, washing and firing). The high strength, lightweight and low thermal conductivity foams can be used as thermal insulating materials to reduce the energy loss of buildings. Due to their high open porosity and specific surface area, foamed AACs can function as catalyst supports in many physicochemical applications.

New scientific results: thesis statements of the doctoral dissertation

1. I have demonstrated that by using different waste materials (treated crumb rubber, blast furnace slag, kaolin wool fibre), alkaline activation and optimizing the rubber/sand ratio, a composite system can be developed with physical properties (compressive strength even 44.0 MPa) comparable to those of the second strength class cements specified in the product standard (EN 197-1).

2. I have concluded that the strength values of waste-based alkali activated cements (AACs) can be maximised by producing and storing specimens in a standard way and size (EN 12390-2). The physical properties of such materials are competitive with those of traditional binders. Moreover, the compressive strength of the developed AAC composite, which contains 2.5 times more waste than the mortar produced from the CEM III slag cement, exceeds the strength value stipulated by the standard for clinker-saving green cement.

3. I have concluded that the compatibility problem between the rubber particles and the AAC matrix could not be remedied either by the superplasticizer commonly used in the cement industry or by hydrophilizing agents proven in the plastics industry. However, the adhesion between the rubber particles and the matrix can be improved by chemical or physical surface treatment of the rubber. The most significant increase in strength (55% improvement compared to the initial value) can be achieved through sulphuric acid treatment. The changes in material structure as a result of the treatment, as confirmed by FT-IR studies, also contribute to the increase in strength of the composite by improving the strength of the rubber particles (Shore A hardness measurement).

4. I have shown that waste-based AAC composites produced by combining sulphuric acid-treated crumb rubber and fibre reinforcement can be used not only in static but also in repetitive load applications, withstand cyclic loading well, and thus the resistance to mechanical stresses can be significantly improved (44.0 MPa → 47.3 MPa, 8% increase in strength).

5. I have demonstrated that the combined technique of saponification/peroxide decomposition/gel casting (SPG) can be used to produce foamed structural materials with a designed porosity and optimum strength. The control of the pore structure can be achieved by a combination of the foaming agent and various stabilizers; by using H_2O_2 solution and by varying the stabilising agent:peroxide (S:F) ratio, AAC foams with a quasi-arbitrarily controllable open porosity (5.8–67.5 vol%) can be produced.

6. I have demonstrated that not only multifunctional foams with controlled properties can be developed, but have also found a solution to prevent the drying shrinkage and consequent severe cracking of the foams, due to the extreme water demand of the aluminosilicate source. In doing so, I developed washing and heat treatment programmes. I have shown that the pre-reduction of the organic matter content (by washing) is critical during the firing of the samples, and that proper heat treatment accelerates the alkali activation reaction, catalyses the decomposition of H_2O_2 and promotes the saponification process, which ultimately leads to an increase in the amount of interconnected and open pores.

7. I have found that the thermal treatment of AAC foams also includes their firing, which not only serves as a method of organic matter removal, but also improves the relevant physical properties, open porosity can be increased by 1/3 and compressive strength by up to 6.5 times.

8. I have confirmed that bulk-type AAC foams have remarkable potential for multifunctional applications and will meet most of the requirements set out for thermal insulation materials and catalyst supports due to their favourable physical properties (compressive strength 8.6 MPa, open porosity 77.7 vol%, bulk density 499 kg/m^3, thermal conductivity 0.041 W/mK, specific surface area 4.3 m^2/g).

9. I have demonstrated that the developed AAC foams themselves have photocatalytic activity (without the binding of metal ions with semiconducting properties on their surface), and have considerable potential in air and wastewater treatment processes due to their pore structure and high specific surface area.

Publications in the field of the PhD thesis

I. Core publications from the PhD thesis work

Publications in international periodicals

1. Boros, A., Varga, C., Prajda, R., Jakab, M., Korim, T. (2021) Development of waste-based alkali-activated cement composites. *Materials,* 14, 5815 (IF: 3,623 (2021)).
2. Boros, A., Korim, T. (2022) Development of geopolymer foams for multifunctional applications, *Crystals,* 12, 386 (IF: 2,589 (2021)).
3. Balczár, I., Boros, A., Kovács, A., Korim, T. (2022) Foamed geopolymer with customized pore structure. *Chemical Industry & Chemical Engineering Quarterly,* 28 (4), 287-296 (IF: 0,925 (2021))

Conference lectures in English with printed abstracts

4. Boros, A., Korim, T., Balczár, I. (2017) Synthesis of inorganic polymers based on different raw materials, *12th Conference for Young Scientists in Ceramics,* Novi Sad, Serbia, October 18-21., ISBN: 978-86-6253-082-0, p. 120.
5. Boros, A., Korim, T., Balczár, I., (2018) Alkali activated cement foams as catalyst supports, *Seventeenth Young Researchers' Conference – Materials Science and Engineering, Belgrade,* Serbia, December 5-7., ISBN: 978-86-80321-34-9, p. 39.
6. Boros, A., Korim, T. (2019) Photochemical activity of metakaolin based geopolymer foams, *13th Conference for Young Scientists in Ceramics,* Novi Sad, Serbia, October 16-19., ISBN: 978-86-6253-104-9, p. 96.

Conference lectures in Hungarian with printed abstracts

7. Boros, A., Balczár, I., Korim, T., (2017) Változtatható porozitású szervetlen polimerek előállítási lehetősége, *XXIII. Nemzetközi Vegyészkonferencia,* Déva, Románia, Október 25-28., ISSN:1843-6293, p. 21.
8. Boros, A., Korim, T., (2017) Kombinált eljárással (GEP) előállított tervezett porozitású alkáli aktivált szervetlen polimer habok, *PhD hallgatók anyagtudományi napja XVII.,* Veszprém, December 04.

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10. Boros, A., Korim, T., (2018) Kaolin alapú AASP habok zsugorodásának és repedési hajlamának csökkentése, *PhD hallgatók anyagtudományi napja XVIII.,* Veszprém, November 26.
11. Boros, A., Korim, T., Prajda, R. (2020) Ipari hulladékanyagok felhasználási lehetőségeinek vizsgálata AAC-bázisú kompozitok előállítására, *PhD hallgatók anyagtudományi napja XX.,* Veszprém, November 16.

Conference poster presentations in English with printed abstracts

12. Boros, A., Korim, T., Balczár, I. (2018) Alkali activated cement foam blends based on metakaolinite and ground granulated blast furnace slag, *14th International Ceramics Congress*, Perugia, Italy, June 4-8.
13. Boros, A., Korim, T., Balczár, I. (2018) Production of inorganic polymer foams with combined foaming process (GSP), *FEMS JUNIOR EUROMAT CONFERENCE 2018*, Budapest, July 8-12.
14. Boros, A., Korim, T., Balczár, I. (2018) Investigation of kaolin based inorganic polymer foams, *11th Chemistry Conference*, Plovdiv, Bulgaria, October 11-13.
15. Boros, A., Korim, T., (2019) Production of crack free catalyst supports from metakaolin based geopolymers, *5th Conference of The Serbian Society for Ceramic Materials*, Belgrade, Serbia, June 11-13., ISBN 978-86-80109-22-0, p. 117.
16. Boros, A., Korim, T., (2019) Special application possibilities of metakaolin based geopolymer foams, *Twenty-first Annual Conference YUCOMAT 2019 & Eleventh World Round Table Conference on Sintering WRTCS 2019,* Herceg Novi, Montenegro, September 2-6., ISBN 978-86-919111-4-0, p. 107.

Conference poster and short oral presentation in Hungarian with printed abstract

17. Boros, A., Korim, T., Balczár, I. (2017) Tervezett porozitású alkáli aktivált szervetlen polimerek előállítása, *XI. Országos Anyagtudományi Konferencia,* Balatonkenese, Október 15-17., ISBN 978-615-5270-40-6, p. 61.

II. Related publications from the PhD thesis work

Publication in international periodical

1. Balczár, I., Korim, T., Hullár, H., Boros, A., Makó, É. (2017) Manufacture of air-cooled slag-based alkali-activated cements using mechanochemical activation, *Construction and Building Materials*, 137, 216-223 (IF: 3,169 (2017))

Publication in Hungarian periodical

2. Eniszné Bódogh, M., Hegedűs-Dobrádi, A., Jakab, M., Korim, T., Soósné Balczár, I., Boros, A., Kovács, A., Kristófné Makó, É. (2021) Nemfémes szervetlen funkcionális anyagok és nanoszerkezetek fejlesztése a Pannon Egyetemen, *Magyar Kémiai Folyóirat,* 127 (3-4), 153-159.

Conference lectures in Hungarian with printed abstracts

3. Boros, A., Korim, T., (2015) Szervetlen polimer bázisú kötőanyagok előállítása alternatív nyersanyagok felhasználásával, *Intézményi Tudományos Diákköri Konferencia Műszaki Tagozat,* Veszprém, November 18.
4. Boros, A., Korim, T., Balczár, I. (2016) Geopolimerek előállítási lehetőségeinek vizsgálata eltérő fajlagos felületű kiindulási komponensek felhasználásával, *Műszaki Kémiai Napok 2016,* Veszprém, Április 24-26., ISBN 978-963-396-087-5, p. 155-156.
5. Boros, A., Korim, T., (2017) Szervetlen polimer bázisú kötőanyagok előállítása alternatív nyersanyagok felhasználásával, *XXXIII. Országos Tudományos Diákköri Konferencia Műszaki Tudományi Szekció,* Dunaújváros, Április 6-8., ISBN 978-963-9915-88-6, p. 64.
6. Balczár, I., Korim, T., Boros, A., Hullár, H. (2017) Hőszigetelő tulajdonságú kötőanyagrendszerek, *XI. Országos Anyagtudományi Konferencia,* Balatonkenese, Október 15-17., ISBN 978-615-5270-40-6, p. 39.
7. Balczár, I., Korim, T., Boros, A., Hullár, H. (2018) Hőszigetelő tulajdonságú kötőanyagrendszerek, *Műszaki Kémiai Napok 2018,* Veszprém, Április 24-26., ISBN 978-963-396-107-0, p. 75.
8. Boros, A., Korim, T., (2019) Rejtett hidraulikus sajátságokkal rendelkező, CaO-ban szegény, természetes bányatermékek alkáli aktiválása, *PhD hallgatók anyagtudományi napja XIX.,* Veszprém, December 02.

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9. Boros, A., Korim, T., Balczár, I. (2016) Comparative Analysis of Inorganic Polymers Obtained by Raw Materials with Different Properties, 4th International Conference on Competitive Materials and Technology Processes, Miskolc-Lillafüred, October 03-07., ISBN 978-963-12-6592-7, p. 143.
10. Boros, A., Balczár, I. Korim, T., Makó, É. (2017) Production of inorganic polymers with different raw material activating methods based on kaolin, *15th Conference & Exhibition of the European Ceramic Society,* Budapest, July 9-13., ISBN 978-963-454-094-6, p. 51-52.

Publication not related to the PhD thesis

Conference poster presentation in English with printed abstract

1. Boros, A., Korim, T., (2017) Analysis of application of lighting technology waste glass for ceramic industry, *Slovak and Czech Glass Conference & Seminar on Defects in Glass,* Trenčianske Teplice, Slovakia, June 28-30.