PRELIMINARY EVALUATION OF LOCAL MINERAL ADDITIONS (BY-PRODUCTS OR WASTES) VALORISATION IN INNOVATIVE CEMENTITIOUS COMPOSITES

Henriette SZILAGYI[1], *Cornelia BAERĂ*[2], *Adrian LĂZĂRESCU*[3], *Anamaria Cătălina MIRCEA*[4]
[1] PhD, NIRD URBAN – INCERC Cluj-Napoca Branch, henriette.szilagyi@incerc-cluj.ro
[2] PhD, NIRD URBAN – INCERC Timişoara Branch, cornelia.baera@incd.ro
[3] PhD Std., NIRD "URBAN – INCERC Cluj-Napoca Branch, adrian.lazarescu@incerc-cluj.ro
[4] PhD Std., NIRD URBAN – INCERC Cluj-Napoca Branch, anamaria.mircea@incerc-cluj.ro

ABSTRACT

Romania's recent joining of the European family implies a fast upgrading of all evaluation references for every direction concerning life evolution and society development, in close correlation with the European ones. In accordance with the European strategies, implemented starting with 2000, sustainability is set as a key priority, governing all further development axes. Innovation, one of the foundation pillars of durability (environmental protection and non-renewable resources management) can be successfully implemented in all fields of activity. For instance, the path to a sustainable infrastructure could include innovative building materials, designed and developed by means of new technologies and of the latest information, as well as the use of additions (industrial waste / by-products), which could contribute to the improvement of their characteristics and performance. The aim of this paper is to present a general overview of the scientific demarches developed in the topic of Material Science, where innovation is achieved by identifying the re-conversion options for wastes and by-products from industrial processes, as mineral additions for cement-based composites.

Keywords: sustainability; innovation; mineral additions (waste or by-products); cement-based composites

REZUMAT

Aderarea recentă a României la familia europeană implică o actualizare rapidă a tuturor standardelor de evaluare pentru direcțiile legate de evoluția vieții și dezvoltarea societății, în corelare directă cu cele europene. În conformitate cu strategiile europene, implementate începând cu anul 2000, sustenabilitatea este stabilită drept prioritatea-cheie, care guvernează toate axele de dezvoltare ulterioară. Inovația, unul dintre pilonii de bază ai durabilității (protecția mediului și gestionarea resurselor neregenerabile) poate fi introdusă cu succes în toate domeniile de activitate. Spre exemplu, calea pentru o infrastructură durabilă poate include materiale de construcție inovatoare proiectate și dezvoltate prin intermediul noilor tehnologii, a celor mai recente informații și utilizarea adaosurilor minerale (deșeuri industriale / subproduse) care pot contribui la îmbunătățirea caracteristicilor și performanțelor acestora. Scopul acestei lucrări este de a prezenta o imagine de ansamblu asupra demersurilor științifice dezvoltate în domeniul Științei și Ingineriei Materialelor, unde inovarea se concretizează prin identificarea opțiunilor de reconversie a deșeurilor și a produselor secundare din procesele industriale ca adaosuri minerale pentru compozite cementoase.

Cuvinte cheie: sustenabilitate; inovare; adaosuri minerale (deșeuri sau subproduse); compozite cementoase

1. INTRODUCTION

Romania's adherence to the European Union implies, among other specified requests, upgrading as well the major standards related to the economic, social, political and industrial development with respect to the UE specific criteria of performance. Consequently, the global principles of Sustainability and Circular Economy should be considered and gradually applied, especially in the industrial area and environment protection, for further optimisation of waste management and natural resources preservation. Developing a sustainable infrastructure by the means of innovative building materials, smart design and technologies represents a large area where these principles can be adapted, verified and potentially valorised.

2. "CIRCULAR ECONOMY" (CE) CONCEPT

2.1. General defining of the CE term

Opposing the traditional, linear model which accepts the waste generating as consequence of production process, the "closing the loop" general approach of the Circular Economy (CE) is based on innovative reconversion of potential waste into raw materials for new purposes (Fig. 1). The advantages are clear, the challenge is identification for possibilities and further on, optimisation of the reconversion route(s).

Fig. 1. The Circular Economy Concept graphical representation (European Commission, 2018)

The key elements that substantiate the CE notion are:

- Prioritizing the Regenerative Resources;
- Waste use as a Resource;
- Preserve & Extend the existing patrimony (goods, equipment, infrastructure, etc.): by life and use extension or new reconversion to another possible destination);
- Cause & Effect Design for Future;
- Digital Technology incorporating;
- Joint value development via collaboration.

2.2. INNOVATION –solution for an improved Romanian infrastructure

Romania nowadays do not comply to the CE model considering the modest recycling processes, reduced natural resource preservation (which constantly grew in the last ten years) and poor innovative concept implementation with actual applicability I the everyday life, beyond the theoretical assumptions. Innovation can signify changing the route from waste generating towards resource, which can be valorised within new products. The synergetic collaboration among all actors on the reconversion play, like, Research and Development, Academia, Industry, Technology and Information market, political will, administrative apparatus, etc. could generate success on this path.

Preliminary evaluation of local mineral additions (by-products or wastes) for their potential in innovative cementitious composites, with improved overall or specified performances, represents practical steps in adapting the CE principles for Romanian particular industrial reality. Developing new materials and further on, principles and methods of valorising several types of mineral additions into cementitious composites represents a complex theoretical and experimental approach, a mix among fundamental, applied and experimental research in the topic of material science. Traditional or innovative investigations and experimental procedures are used and adapted for a large overview on the obtained results, for a clear understanding of their real and critical potential as new materials: bearing capacity, durability, and efficiency in terms of economic reliability with respect to the traditional ones.

3. VALORISING THE MINERAL ADDITIONS IN CEMENT-BASED MATERIALS

All around the world concrete and cement-based material are the most widely used building materials. Their intense use in the construction industry generate a big consumption and request for cement, essential binging element in their structure. It is well known that cement carbon footprint, estimated at about 0.8 – 1.1 tons of CO_2 emissions for each tone of cement, do not make cement an environmental friendly material. As consequence, intense efforts are generally performed for its partial replacement as binding element in concrete and cementitious composites, without altering their performances, but on the contrary, increasing them. Mineral additions, mainly powders, are added to the matrix, proving a beneficial effect to the mixes, especially in the special concrete development: self-compacting concrete, high strength concrete, high performance fibre reinforced cementitious composites (HPFRCC), etc. (Szilágyi, 2011).

Along time, it was scientifically proven by the means of many theoretical and experimental studies, the beneficial influence of fine powder additions to both, fresh state and also hardened state properties of cementitious materials; there is a cumulative state of reactive effects on the matrix, of chemical and physical nature, generating beneficial changes in the regular course of concrete mixing, setting, hardening and also mechanical and durability performing during its service life. The chemical effect is mainly related to the stimulation of hydration and pozzolanic reactions, distinct but both of them generating the C-S-H products which determine the matrix hardening and further on, the strength of the material. The physical effect of optimizing the matrix "packing", for better voids filling by the means of small size particles of fillers, determine clear alteration of composite heterogeneity and, as consequence, superior mechanical and long term, durability performances. These effects are also clear fructified in case of self-compacting concrete (Larbi, 1993; Hunger et al., 2008; Pop et al., 2015).

4. MINERAL ADDITIONS DERIVED FROM LOCAL INDUSTRY

Many industrial processes from metallurgy, energetic, natural stone processing industries, mining branches, etc., are generating mineral by-products or waste materials like limestone powders or slurries, slags, fly ash or silica fume etc., as secondary products of their main targets. Most of these secondary products could be evaluated and reused, in accordance to their potential, for instance as additions to specific concrete or cement-based composites (Szilágyi et al., 2018).

The process for identifying the potential materials (waste and as well by-products which are not entirely valorised and consequently turn unavoidably into waste), generated by local industry and establishing their potential use as mineral additions to concrete, represents a complex process that has to consider a multitude of variables and also a lot of inter-connected and successive activities: identifying the industry causing the waste/by-products that could fit the purpose, preliminary evaluation of the potential addition and identifying the type of composite they could be compatible to, mapping of resources/similar resources, estimation of waste generated/industry type, etc. The next steps are related to mixes testing development, by using the potential mineral additions to and in comparison to the established reference, for proper preliminary evaluation of their actual influence in the mixes: weak points and strong points.

The preliminary investigation performed within the current research programme generally focused on three types of materials, wastes and also by-products:

a) Fly Ash (FA), derived from two distinct Romanian Power plants: CET Govora and CET Mintia (By-product with high risk of waste becoming);
b) Boiler Slag (BS) (resulted from CET Govora) - waste;
c) Limestone Slurry (LS), (local source) - waste.

5. FLY ASH (FA) – A MAJOR OBJECTIVE OF INVESTIGATION

5.1. Fly ash (FA) – industrial by-product for cementitious composites

It is generally known that fly ash (FA) is a by-product resulted from burning pulverized coal for electricity production: the non-combustible impurities in the coal (e.g. clay, quartz, feldspar, dolomite, limestone etc.) are turned into glassy, spherical particles that are not released in the atmosphere for easily understandable, ecological reasons; they are captured by the help of special filter system resulting the fly ash (FA) (Xu and van Deventer, 2000; Anuradha et al., 2012; Van den Heede, 2014). Fly ash, considered to be an artificial pozzolan (with elements reacting with Ca^{2+} or $Ca(OH)_2$ in humid environment, generating new binding products), can be classified according to ASTM C618-12a, as follows:

- Class F fly ash (with mainly pozzolanic potential); it is characterized by a low CaO content (<10%) and substantial SiO_2 and Al_2O_3 compounds. It is the most wide-spread type of FA.
- Class C fly ash (with both pozzolanic and hydraulic properties).

It is scientifically proven that FA's pozzolanic reactivity depends significantly on its glass content. It was also noticed that FA properties differ considerably, function of the production process: coal type, the burning technology, the fuel type and, as consequence, function of the resulting oxide profile and grain size distribution (Lăzărescu et al., 2017; Lăzărescu et al., 2018).

Integrated pollution prevention and control in the European Union, by the means of a corresponding Directive, has as main target pollution reduction regarding power plants and the waste type and quantity they are producing, imposing strict demands related to the filtering and collecting system and the gas emissions in the atmosphere. Additionally, supplementary efforts are performed for fly ash proper collecting and use as by-product, in cement industry and also in concrete and cementitious composites production, in order to avoid the landfill forming in the coal power plant neighbourhood, with ecological and environmental negative impact. Immediate collecting of the fly ash and proper storage and use makes it a valuable by-product, with positive effects for fresh and hardened state as well of cement based composites; other fields of direct application were also identified (cement production, road infrastructure-soil stabilizing binder, etc.) but they are not the topic of the current study. As soon as the fly ash is not valorised and it is placed in landfills, its properties are dramatically compromised and its potential use as well.

5.2. Fly ash (FA) in Romania

There is still the large production of fly ash on Romanian territory, result of many coal power plants still functional, part of them in the process of improving the ecological aspects of their production (Fig. 2); consequently, fly ash becomes the major topic of the current study, with increased interest for its evaluation and potential use in innovative cement-based composites.

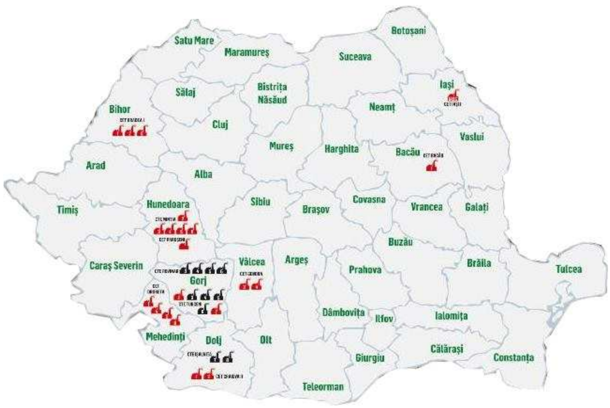

Fig. 2. Map of coal fired power plants distribution in Romania and their functioning with respect to environmental requests: red colour – improper functioning; black colour – improved functioning (Rădulescu, 2016)

Several types of fly ash were investigated, from two different sources: Mintia CET and Govora CET.

The sampling of the four types of Govora CET fly ash was performed by an Incerc Cluj-Napoca team, directly at the coal power plant location (near Râmnicu Vâlcea, Vâlcea County) (Fig. 3).

The sampling inspection of the research team was performed in-situ for a better understanding of the whole system: raw material source and influence over the resulting FA, production process, FA filtering, collecting and storage, resource use, local waste management, the state of synergetic industries cooperation as part of re-use techniques implementation etc. as strong request of CE concept.

Fig. 3. Device for fly ash capture – technological flow – Govora CET

Four different types of fly ash were collected from the Govora CET production site (Fig. 4): a) Concrete addition type FA (for concrete mixes); b) Cement addition FA (for cement production); c) FA collected directly from the electro filter of the capturing system of the power plant; d) Eco-Par FA (coarse particle FA for road infrastructure).

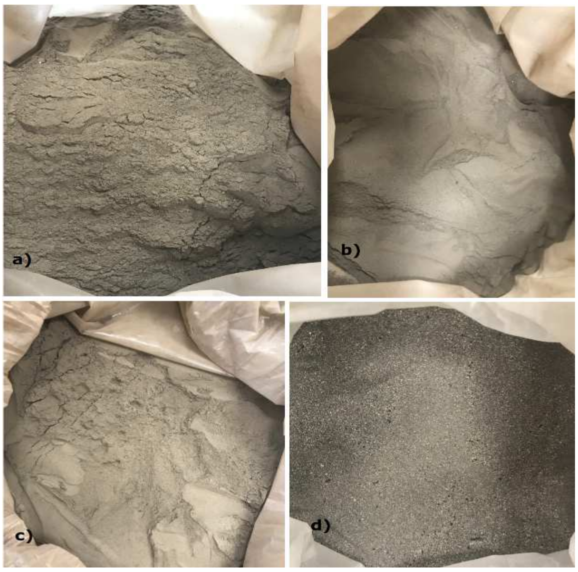

Fig. 4. Four types of FA, sampled from the Govora CET production site

The main differences between the a, b and c types of Govora fly ash types in the grain size distribution: a) the Concrete FA is a finer grain powder (N type), destined as II type addition for concrete mixes; b) the Cement type FA is a by-product destined to Cement factories as direct addition in certain cement types; c) the FA material sampled directly at the base of the electro filter collecting device represents a raw combination of a and b types, before sorting according to the grain size distribution through specific technological means. It was collected for a quick performance comparative test as direct addition to cement based composites, in order to possibly eliminate the additional grain size filtering, applied for a and b types, and possibly cost reducing for the final product.

The fourth type of fly ash, Eco-par, represents a coarse powder with direct destination in the road infrastructure as, soil stabilising binder. It was mainly considered for a comparative evaluation of the general potential of Govora CET fly ash.

The a, b and d types of Govora fly ash represent by-products, with already identified potential of re-use in the cement industry, concrete production or road infrastructure development, as already specified. Immediately after the collecting process they are stored in specific siloes, where from the delivery is easily ensured in accordance to the demand.

The main identified problem is the low rate demand for such by-products, covering just a reduced percent of the entire FA production. The FA by-products are collected function of the estimated, but still reduced demand from the specified industrial fields, the rest of it becoming waste landfilled fly – ash, stored in the neighbourhood of the plant.

Fig. 5. Fly ash (FA) and Boiler Slag (BS) landfills from Govora CET (Impactul sectorului energetic asupra mediului, 2018)

To the obvious devastating environmental impact generated by such intrusive landfills (Fig. 5), with potential dangerous leaching in soil and underground water, increased radioactivity, nature deteriorating, landscape aesthetics compromising, etc., it is added the substantial waste of such valuable, silica reach, mineral addition with clear valorising potential for the construction industry and infrastructure. Therefore, the increased interest for re-use and waste prevention, as developed within the present study (that discovers re-integration fields before the by–product degenerates into waste), are simple solutions towards a practical adherence to the Circular Economy functional system.

5.3. Boiler Slag (BS), secondary waste of coal power plant

The Boiler Slag (BS) represents a secondary waste product, resulted from the process of coal burning for electricity production in a coal power plant. Such a material waste was identified during the sampling, FA main targeted, visit at Govora CET. (Fig. 6, b).

Distinct from the fly ash (fine grain powder), the boiler slag represents a coarse, non-homogeneous material, resulted from the bottom part of the furnaces during the burning process (Fig. 6, a).

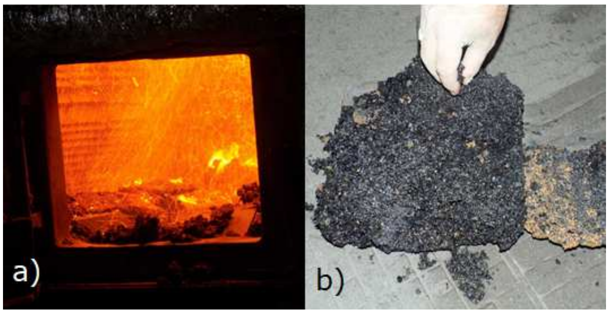

Fig. 6. Boiler Slag (BS) from Govora CET: a) incandescent material at the end of the process; b) cooled material, before storage

There is no information about previous experimental studies regarding the potential re-use of Govora BS in cement based mixes. Consequently, a preliminary investigation is elaborated during this present study. The raw material (Fig. 7, a) is considered as potential aggregate replacement in concrete. Consequently, the raw material is initially sieved and divided in specific granular classes: coarse grains, rest on 4 mm sieve (Fig. 7, b), 2/4 granular class (Fig. 7, c); 0/2 granular class (Fig. 7, d). After careful consideration it was decided that the 0/2 granular class BS would be used as addition in the further developed mixes.

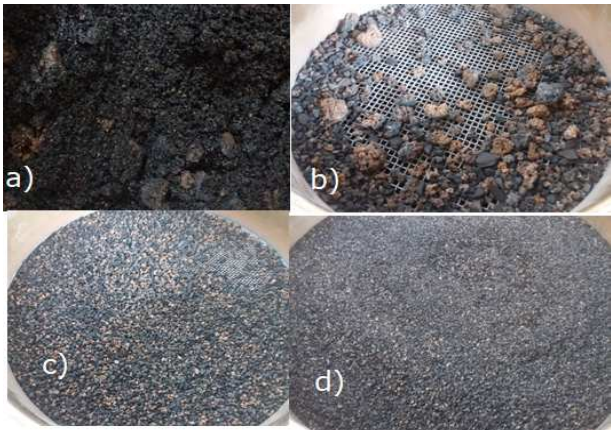

Fig. 7. Boiler Slag (BS) from Govora CET

5.4. Slurry lime stone (SL)

Limestone is traditionally known as a beneficial mineral addition to the cementitious composites, both in fresh state, regarding the workability of the material, and hardened state as well, considering an improved matrix packing that generates superior mechanical and durability performance (Szilágyi et al., 2017).

Limestone fillers, despite their inert character, were proved to bring positive effects to the cementitious mixes: fresh mix bleeding prevention, better consistency and cohesion of the mix and also good mechanical behaviour (Baeră et al, 2017).

Fig. 8. Limestone Slurry (LS) waste material from local source (Resido SRL, Cluj-Napoca)

The evaluated Limestone Slurry (LS) is a waste material resulted from the production process of a local (Cluj-Napoca Region) factory for natural stone processing, namely

Resido SRL. The LS material is stored in a landfill in the vicinity of the production location, as waste (Fig. 8).

Till now, there was no study regarding potential valorising of the Limestone Slurry waste material; consequently, the current research program comes as a first trial study in this area, offering potential solutions for the SL re-use and re-integration as raw material for new construction products.

The optimum approach considers SL waste processing costs reduced as much as possible; in order to realise that, the first approach, of slurry conversion into dry powder, which requires drying process and resource consumption, was replaced by simply adding the raw SL into mixing, after careful determination of the paste water content, for proper control of the liquid in the concrete mix.

6. INNOVATIVE CEMENTITIOUS COMPOSITES WITH MINERAL ADDITIONS: MAIN RESEARCH DIRECTIONS

The general approach regarding the development of innovative cementitious composites by using mineral additions (waste or by-products) consists in comparative analyses between the reference and the new mix(es) designed with specific replacement(s) / additions.

The complexity of the study is revealed by the three typologies of materials developed by using the previous mentioned mineral additions, mostly as cement (partial or complete) replacement:

- FAGPP - Geopolymer composites (pastes or mortars): the concept of Alkali Activated Materials (AAM) is used for complete replacement of cement with fly ash (FA), in mixes with mechanical performance similar as cementitious materials (Lăzărescu et al., 2017; Lăzărescu et al., 2018);
- HVFA - Cementitious composites from the category of high volume fly ash concrete, developed considering reliable, consecrated research in this field (Van den Heede, 2014);
- ECC (Engineered Cementitious Composites), with an increased FA content in the binding system with respect to the cement content: FA/C > 1.0, also developed considering previous research in this topic (Li, 2008; Li and Herbert, 2012; Yang et al., 2009; Snoeck, 2015; Baeră, 2016; Baeră et al., 2016a; Baeră et al., 2016b; Baeră et al., 2017).

7. CONCLUSIONS

The wastes and by-products use as additions in cement-based materials for construction industry is not new, but its innovative approach relies in its constant adaptability to the real industrial demand: potential need of certain types of materials and waste evaluation. The constant follow-up from the technological transfer networks, by the help of modern techniques for communication and evaluation, encourage significantly the on-going scientific investigation at INCERC Cluj.

The comparative analyses of the developed mixes, in terms of bearing capacity and durability performance, represent on-going research in the topic of mineral additions for cement based innovative materials.

ACKNOWLEDGEMENTS

This paper is supported by the Programme *Research for Smart Specialization, Sustainable Territorial Development, Environment Preservation and Resilience of Building Heritage* - "CONCRET", Programme code: PN 18 35 04 03: "Research for valorising the inert, hydraulic, late or pozzolanic mineral additions in innovative cementitious materials for resilient structures, in the context of implementing the "Circular Economy" concepts in Romania, financed by the Romanian Government.".

REFERENCES

1. Anuradha, R., Sreevidya, V., Venekatasubramani, R., Rangan, B.V., *Modified guidlines for geopolymer concrete mix design using Indian standard*, Asian Journal of Civil Engineering (Building and Housing), 13(3): 353-364, 2012.

2. Baera, C., *Self-Healing capacity of advanced engineered cementitious composites*, PhD Thesis, Technical University of Cluj-Napoca, 2016.
3. Baeră, C., Szilágyi, H., Mircea, C., Hegyi, A., Snoeck D., *Fibre engineered cementitious materials (FECM) optimisation by the use of hybrid polypropelene fibres and supplementary powder addition*, Proceedings of the 17th International Multidisciplinary Scientific GeoConference & EXPO – SGEM 2017, Albena, Bulgaria, 27.06.-06.07.2017, vol. II, Nano, bio and green – technologies for a sustainable future, ISBN 978-619-7408-13-3, ISSN 1314-2704, pp. 169-176, 2017.
4. Baeră, C., Păstrav, M., Szilagyi, H., German, O., Constantinescu, H., *Fibre engineered cementitious materials (FECM) as beam to column monolithic interface within seismic resistant hybrid joint*, Proceedings of the 16th International Multidisciplinary Scientific GeoConference & EXPO – SGEM 2016, Albena, Bulgaria, 28.06.-07.07.2015, vol. II, Nano, bio and green – technologies for a sustainable future, pp. 105-112, 2016a.
5. Baeră, C., Snoeck, D., Szilagyi, H., Mircea, C., De Belie, N., *Dynamic loading performance of fibre engineered cementitious materials with self-healing capacity (SH-FECM)*, Proceedings of the 16th International Multidisciplinary Scientific GeoConference & EXPO – SGEM 2016, Albena, Bulgaria, 28.06.-07.07.2015, vol. II, Nano, bio and green – technologies for a sustainable future, pp. 91-98, 2016b.
6. European Commission Report: Critical Raw Materials and the Circular Economy, https://ec.europa.eu /commission/publications/report-critical-raw-materials- and-circular-economy_en.
7. *Impactul sectorului energetic asupra mediului*, http://www.scritub.com/geografie/CONDITIILE-DE-MEDIU-IN-OLTENIA1321221015.php, webpage, retrieved 2018.
8. Larbi, J.A., *Microstructure of the interfacial transition zone around aggregate particles in concrete*, Cement and Concrete Research, 19(2): 161-172, 1993.
9. Lăzărescu, A., Szilagyi, H., Baeră, C., Ioani, A., The *Effect of Alkaline Activator Ratio on the Compressive Strength of Fly Ash-Based Geopolymer Paste*, IOP Conference Series: Materials Science and Engineering, 209, 2017.
10. Lăzărescu, A., Szilagyi, H., Ioani, A., Baeră, C., *Parameters Affecting the Mechanical Properties of Fly Ash-Based Geopolymer Binders – Experimental Results*, IOP Conference Series: Materials Science and Engineering, 374, 2018.
11. Li, V.C., *Engineered Cementitious Composites (ECC) Material*, Structural, and Durability Performance Concrete, Concrete Construction Engineering Handbook, Chapter 24, Ed. E. Nawy, CRC Press, 2008.
12. Li, V.C., Herbert E., *Robust self-healing concrete for sustainable infrastructure*, Journal of Advanced Concrete Technology, 10(6): 207-218, 2012.
13. Pop, I., De Schutter, G., Desnerck, P., Szilagyi, H., *Influence of self-compacting concrete fresh properties on bond to reinforcement*, Materials and Structures Journal, 48(6): 1875-1886, 2015.
14. Rădulescu, C., *The state of the Romanian coal fired power plants in 2016*, GREENPEACE Report, pp. 16-18, 2016.
15. Snoeck, D., *Self-healing and microstructure of cementitious materials with microfibres and superabsorbent polymers*, PhD Thesis, Ghent University, 2015.
16. Szilágyi, H., *Betoane speciale*, Ed. Napoca Star, Cluj-Napoca, Romania, 2011.
17. Szilágyi, H., Baeră, C, Hegyi, A., Lăzărescu, A., *Romanian resources of waste and industrial by-products as additions for cementitious mixtures*, Proceedings of the 18th International Multidisciplinary Scientific GeoConference & EXPO – SGEM 2018, Albena, Bulgaria, 27.06.-06.07.2018, Vol. II, Nano, Bio AND Green – Technologies for a Sustainable Future, 2017, ISBN 978-619-7408-13-3, ISSN 1314-2704, pp. 325-332, 2018.
18. Szilágyi, H., Baeră, C., Păstrav, M., Gherman, O., Constantinescu, H., *Designing self-compacting fibre reinforced concrete compositions by optimal materials synthesis*, Proceedings of the 17th International Multidisciplinary Scientific GeoConference & EXPO – SGEM 2017, Albena, Bulgaria, 27.06.-06.07.2017, vol. II, Nano, Bio AND Green – Technologies for a Sustainable Future, 2017, ISBN 978-619-7408-13-3, ISSN 1314-2704, pp. 81-85, 2017.
19. Van den Heede, P., *Durability and sustainability of concrete with high volumes of fly ash*, PhD thesis, Ghent University, Ghent, Belgium, 2014.
20. Xu, H., van Deventer, J.S.J., *The Geopolymerisation of Alumino-Silicate Minerals*, International Journal of Mineral Processing, 59(3): 247-266, 2000.
21. Yang, Y., Lepech, M.D., Yang, E.H., Li, V.C., *Autogenous healing of engineered cementitious composites under wet–dry cycle*. Cement and Concrete Research, 39(5): 382-390, 2009.