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Research challenges for broader application of alternative binders in concrete

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Subject review

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Research challenges for broader application of alternative binders in concrete

Rapid population growth and urbanisation have imposed the need to develop more sustainable construction solutions in line with the seventh basic requirement for construction works - sustainable use of natural resources. One of the strategies is to use materials available in abundant quantities to create alternative binders for concrete. An opportunity in this dynamic field is the availability of numerous types of by-products and waste materials, which can be used for the development of various types of alternative binders. The aim of the paper is to pinpoint some scientific challenges that need to be dealt with to ensure broader application of alternative binders in engineering practice.

Key words:
sustainability, durability, alternative binders, microstructure, practical application

Pregledni rad

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Istraživački izazovi za širu primjenu alternativnih veziva u betonu

Brz rast stanovništva i urbanizacija doveli su do potrebe za razvojem održivijih građevnih rješenja u skladu sa sedmim temeljnim zahtjevom za građevine - održivim korištenjem prirodnih resursa. Jedna od strategija je korištenje materijala dostupnih u dovoljnim količinama za pripremu alternativnih veziva za beton. Prilika u ovom dinamičnom području je dostupnost brojnih vrsta nusproizvoda i otpadnih materijala koji se mogu koristiti za razvoj različitih vrsta alternativnih veziva. Cilj rada je naznačiti neke znanstvene izazove koje je potrebno riješiti kako bi se osigurala šira primjena alternativnih veziva u inženjerskoj praksi.

Ključne riječi:
održivost, trajnost, alternativna veziva, mikrostruktura, primjena u praksi

Übersichtsarbeit

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Forschungsherausforderungen für die breitere Anwendung alternativer Bindemittel in Beton

Das rasche Bevölkerungswachstum und die Verstädterung haben dazu geführt, dass nachhaltigere Gebäudelösungen entwickelt werden müssen, die dem siebten Grundbedarf an Gebäuden entsprechen - der nachhaltigen Nutzung natürlicher Ressourcen. Eine der Strategien besteht darin, die verfügbaren Materialien in ausreichenden Mengen zu verwenden, um alternative Bindemittel für Beton herzustellen. Eine Gelegenheit in diesem dynamischen Bereich ist die Verfügbarkeit zahlreicher Arten von Nebenprodukten und Abfallmaterialien, mit denen verschiedene Arten von alternativen Bindemitteln entwickelt werden können. Ziel der Arbeit ist es, einige der wissenschaftlichen Herausforderungen aufzuführen, die angegangen werden müssen, um eine breitere Anwendung alternativer Bindemittel in der technischen Praxis zu gewährleisten.

Schlüsselwörter:
Nachhaltigkeit, Haltbarkeit, alternative Bindemittel, Mikrostruktur, praktische Anwendung

1. Introduction

Concrete is the world's most used construction material (and, in general, the second most frequently used material after water), with over 25 billion tons of concrete used worldwide each year [1]. Traditional concrete industry is based on the linear model, i.e. large amounts of non-renewable resources are utilised during production, and significant emissions are caused. In addition, at the end of service life, considerable energy is used for demolition, with generation of waste and further emissions. Cement alone contributes to approximately 96 % of the carbon footprint of concrete, and 85 % of the embodied energy [2]. In 2015, the total mass of cement produced was 4.6 billion tonnes [3, 4]. This is equivalent to about 626 kg of cement/per capita, a value higher than the amount of human food consumption [5]. The global average CO_2 emission per tonne of cement manufactured is estimated at approximately 0.83 tonnes [6], meaning that the production of ordinary Portland cement accounts for 5 % of world-wide CO_2 emission.

The global population is expected to reach between 8.3 and 10.9 billion by 2050. Rapid population growth follows increased demand for clean water, air, land and need of housing and infrastructure. In a case where construction industry continues with "business as usual", considering the expected production increase, in 2050 cement industry alone will contribute to 24 % of total global CO_2 emission [7]. Such high share of CO_2 emission for one industry alone will not be tolerated as the world acts to stabilise atmospheric pollution. To meet the growing needs for urbanisation and to comply at the same time with European goals for the protection of natural resources and reduction of emissions, there is a strong motivation to develop more sustainable construction solutions with a lower environmental impact, in line with the 7th basic requirement for construction works - sustainable use of natural resources [8]. Considering that any improvement in cement, due to its dominant share in carbon footprint, can lead to a significant savings, most scientific efforts are presently focussing on the development of alternative binders for concrete (ABC).

Many types of cement are already available on the market, especially when one considers that there is a limited combination of materials that are used in industrial production of cement. At the same time, the potential of using numerous other materials as partial or total cement replacement is studied, which could lead to creation of an enormous number of new binders that could at some point become available on the market. This on one side presents a great opportunity in this dynamic field. However, new binders could significantly differ from classical cement, and could lead to different concrete properties on the macro scale. Vast number of combinations with different chemical and physical properties compared to classical cement concrete opens different scientific challenges that need to be tackled before introducing wider application of alternative binders in the engineering practice.

2. Opportunities

2.1. Possible alternative binders for concrete

Alternative binders for concrete form a new generation of construction materials that constitute a sustainable and economical alternative to ordinary Portland cement. Considering the vast societal challenges and huge amount of material at stake, it is obvious that there is no single solution to this problem and that all research knowledge must be mobilised. The list of potential ABCs is steadily growing, but some of the most promising candidates are listed below.

2.1.1. High volume supplementary cementitious materials (SCM)

Cement containing small amount of supplementary cementitious materials already make up a large majority of currently produced cementitious binders. The global clinker factor was estimated at 0.77 in 2015, which means that at least 800 Mt of SCMs was used on a total of 4200 Mt cement produced in that year [9]. To create a more significant ecological effect, a push toward high-volume SCMs is inevitable [10], and involves development of binders based on SCMs with small amount of cement used as an activator [11]. To meet a growing demand for cement and concrete, and considering limited supplies of high-

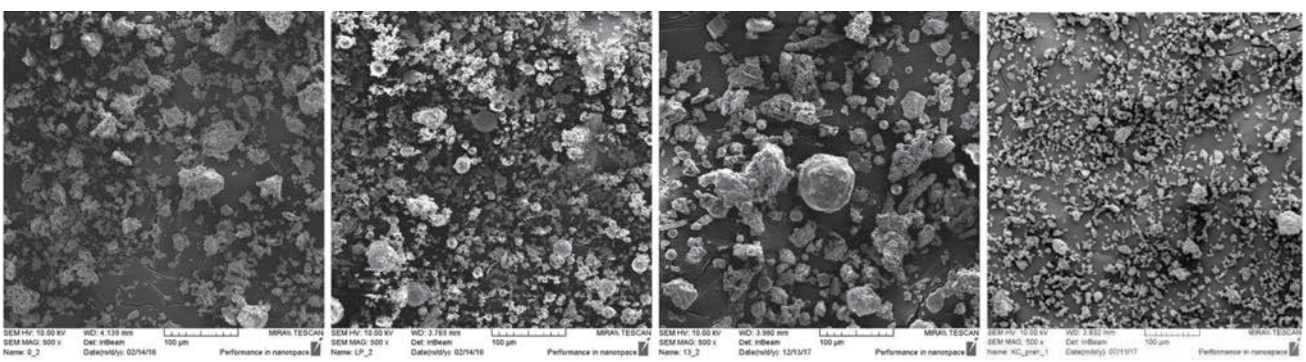

Figure 1. Comparison of size and shape of particles of (from left to rigth) cement, fly ash, biomass ash and incinirated sewage sludge ash [15, 19]

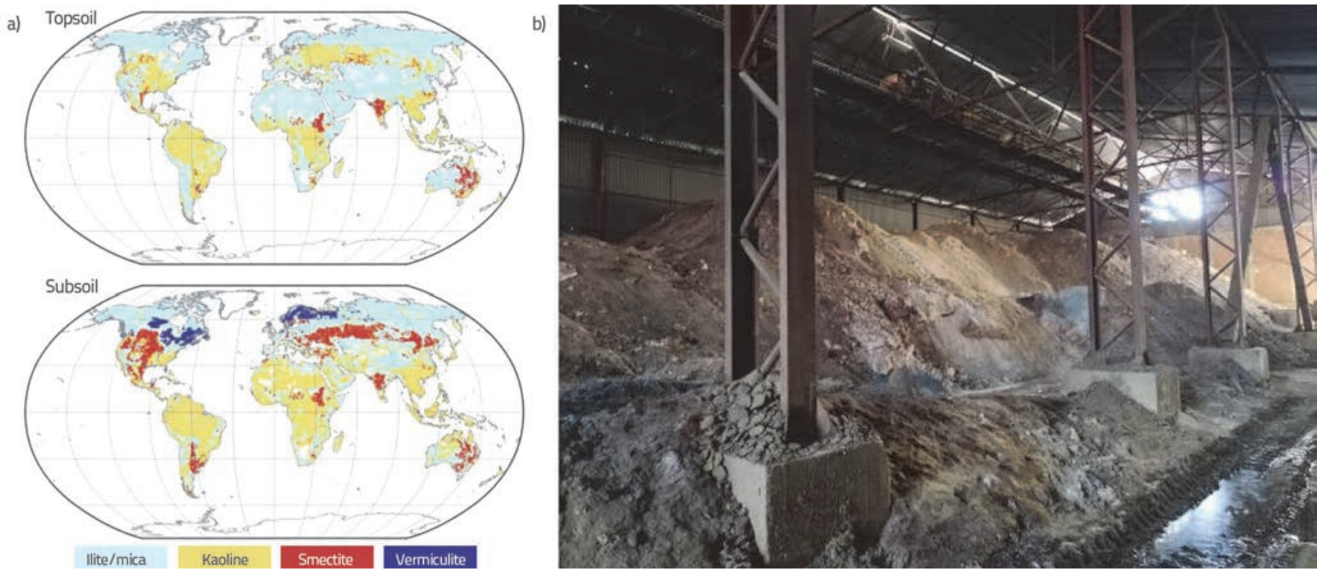

Figure 2. a) Distribution of the most abundant clay-size mineral group in each grid cell around the world, nicely coinciding with the parts of the world in need of massive construction [24]; b) Stockpiling of clay in Topusko, Croatia

quality SCMs, research is focussed at alternative SCMs such as red mud [11, 12], biomass ash [13-15], copper slag, calcined clays [16], limestone [17], and their engineering combinations [18]. The main challenge is to find materials that are available in significant quantities and that have favourable chemical and physical properties (such as particle size distribution presented in Figure 1) for use as mineral addition to cement.

2.1.2. Limestone calcined clay cement (LCC)

Limestone is normally used as filler in cement industry; however, in recent years, it started to be used as a partial replacement for ordinary Portland cement [20]. One of the methods of activating reactivity of limestone is adding reactive and silica-rich and alumina-rich materials, such as calcined clays [21, 22]. In countries with an established ceramic industry substantial reserves of suitable clays are currently stockpiled as waste [23].

Looking at the map presented in Figure 2.a it can be observed that the clay most favourable for application in binder (kaolinite) is abundant mostly in regions where there is a massive need for construction, which makes the idea of unleashing this clay use potential highly justified. Currently, research efforts are focussed on pinpointing types of clays whose calcination would yield the most reactive material with an acceptable ecologic footprint. Reserves of clay available as waste in the region of Topusko in Croatia are shown in Figure 2.b.

2.1.3. Alkali activated materials (AAM)

Alkali activated materials can be any binder system derived by reaction of an alkali metal source (activator) with a solid silicate powder (precursor) [25], such as fly ash and slag [26, 27], ferronickel slag [28], red mud [29], calcined clay [30], etc. The activators are soluble substance that supply alkali metal

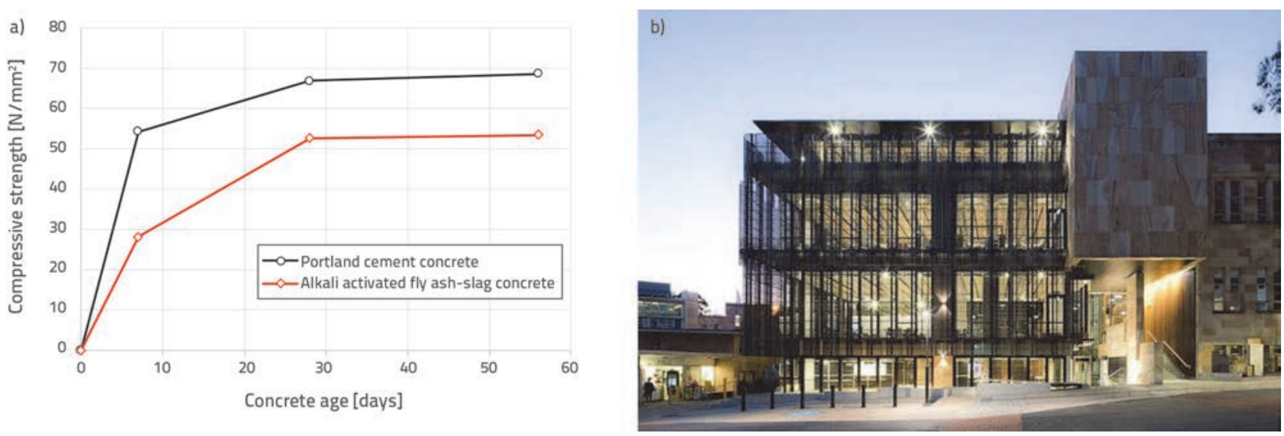

Figure 3. a) Compressive strength of OPC and alkali-activated fly ash-slag concrete [31]; b) Queensland's University GCI building with 3 suspended floors made from geopolymer concrete [32]

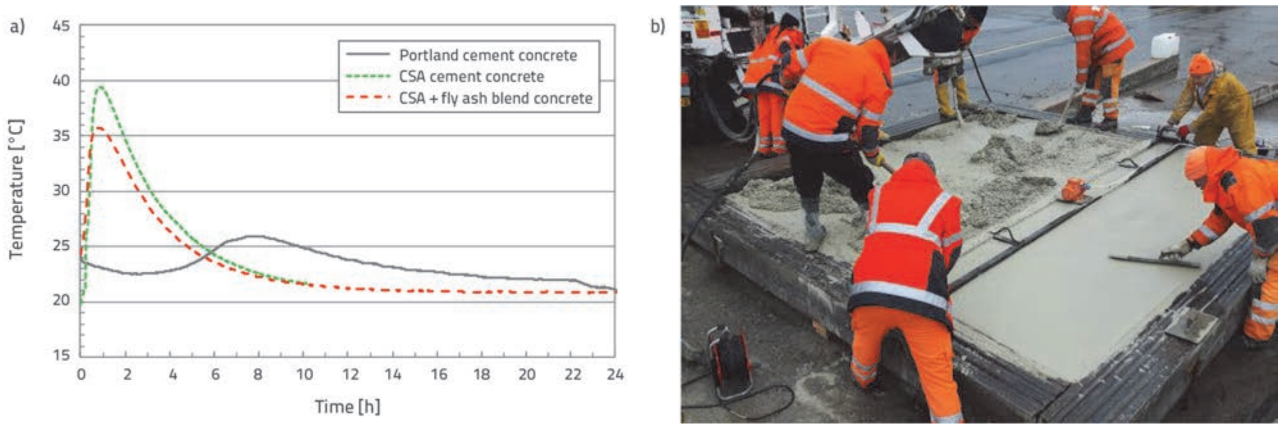

Figure 4. a) Comparison of temperature development of Portland cement concrete, CSA cement concrete and CSA and fly ash blend concrete during 24 hours [37]; b) Placement of CSA cement based concrete on airport runway (photo curtesy: T. Conjar, TPA)

cations, raise pH of the mixture and accelerate the dissolution of solid precursor. Figure 3.a shows an example of compressive strength testing for concrete prepared with 370 kg of CEM I per one cubic meter of concrete and 0.42 water to cement ratio, on the one side, and with mix of 340 kg of fly ash and 85 kg of slag per one cubic meter of concrete activated with water glass and NaOH. Considering that the second mix is truly cement free, the compressive strength result of over 50 N/mm^2 is quite remarkable. Figure 3.b shows an example of structural application of geopolymer concrete on Queensland's University GCI building. Challenges in the field of AAM use lie in the fact that activators are industrially produced chemicals, and do require special attention during handling. Thus, the quantity of activators needed to obtain satisfactory properties of resulting concrete should be minimised. Another challenge lies in the fact that currently the most developed AAM are based on fly ash and slag. It is generally accepted that, on the global scale, the quantities of these materials are insufficient to fully substitute total cement consumption with AAM. Therefore, AAM will probably hold only a percentage of the market of sustainable construction materials in the future.

2.1.4. Calcium sulfoaluminate cement (CSA)

Calcium sulfoaluminate are based on two types of clinkers: sulphoaluminate belite clinker and ferroaluminate clinker [33, 34], in which different amounts of calcium sulphate are added [35]. CSA cements are based on three raw materials - limestone, bauxite and calcium sulphate, and current research efforts are focussing on replacing some of these materials with industrial waste and by-products. Materials of special interest are fly ash [36], blast furnace slag, phosphogypsum, electric arc furnace slag, red mud and flue gas desulfurisation gypsum, etc. CSA cements have very fast reaction time (Figure 4.a), leading to fast strength gain, which makes them ideal for application where load bearing capacity in early ages is needed, such as airport runways (Figure 4.b).

Table 1. First estimate of availability of relevant secondary raw materials for ABCs [38, 39]

Type	Location	Quantities
Fly ash	Plomin TE, Croatia	70,000 tons/year
	Šoštanj TE, Slovenia	1 million tons/year
	Nikola Tesla TE, Serbia	5.5 million tons/year
	TE Kakanj and Tuzla, BiH	800.000 tons/year
GGBS	Zenica, Bosnia & Herzegovina	650.000 tons/year
BOF slag	Zenica, Bosnia & Herzegovina	150.000 tons/year
Electric arc furnace steel (EAFS) slag	Jesenice, Slovenia	about 150 kg /1 ton of steel
	Sisak, Croatia	1.5 million tons, landfilled
	Split, Croatia	30,000 tons, landfilled
Silica fume	Jajce, Bosnia & Hercegovina	10,000 tons/year
Red mud	Dobro selo, B&H	10 million tons, landfilled
	Podgorica (KAP), Montenegro	7 million tons, landfilled
Flue gas desulphurisation gypsum	Slovenia	400,000 tons/year
Phospho gypsum	Lonja field, Croatia	300,000 tons landfilled
Ferronickel slag	Macedonia	1.13 million tons/year
Copper slag	Serbia	23 million tons landfilled
	Bulgaria	700.000 tons/year
Wood ash	Croatia	25.414 tons/year
Limestone	Exploitation sites in Croatia	approx. 150 mill. tons reserve
Clay	Exploitation sites in Croatia	approx. 4 mill tons of reserve

Figure 5. Examples of stockpilling industrial waste materials: a) slag landfill, b) fly ash landfill, c) red mud landfill

2.2. Available raw materials in the region

To be used in a binder, a raw material needs to have properties that are comparable to cement properties, such as particle size distribution, chemical composition and solubility / stability in water. Since cement is basically composed of silicon, aluminium, iron, calcium, sodium, potassium and magnesium oxides, it is raw materials based on these oxides, with a potential to form hydrates with cementing properties, that are of interest. When looking for potential sources, it becomes obvious that there are numerous industries that create by-products exhibiting exactly these properties.
As a first step in the development of ABC with regional materials, appropriate sources must be identified. The first estimate of availability of relevant secondary raw materials in the region is presented in Table 1.

The locally identified materials currently present environmental burden for the named industries, since they are mostly landfilled near the plant. These landfills will soon become not only environmental but an economic burden as well. Furthermore, there are many examples of environmental catastrophes resulting from poorly controlled landfilling. A recent example is the spilling of red mud around villages in Hungary [40]. By finding possible uses of industrial waste products as raw materials for preparation of alternative binders for concrete, it is possible to avoid ecological problems (which could lead to environmental disasters) and high landfill costs (which could lead to increase in energy or material costs). Examples of landfilling of raw materials obtained as by-products are presented in Figure 5.a, 5.b and 5.c, which shows landfilling of slag from steel production, fly ash from a thermal power plant, and red mud from aluminium production.

Table 2. Relative availability in the region and possible applications of different materials

Type of raw material	Quantities available in the region	Possible alternative binders			
		SCM	AAM	CSA	LCC
Fly ash	■■■	x	x	x	
GGBS	■■■	x	x	x	
BOF slag	■	x	x	x	
Electric arc furnace steel slag	■	x	x	x	
Silica fume	■	x			x
Red mud	■■■■	x	x	x	x
Flue gas desulfurization gypsum	■			x	
Phosphogypsum	■			x	
Ferronickel slag	■■	x	x	x	
Copper slag	■■■	x	x		
Wood ash	■■	x	x		
Limestone	■■■■■	x			x
Clay	■■■■■	x			x

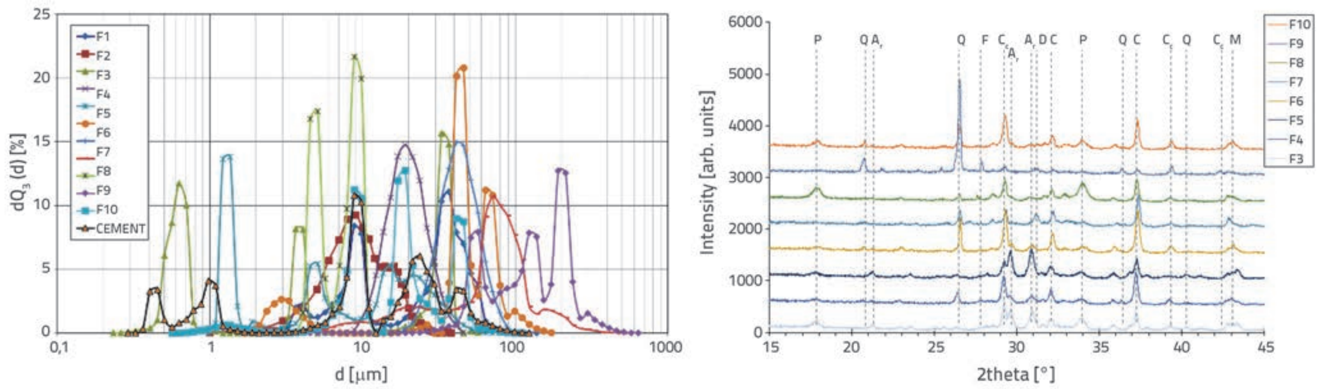

Figure 6. Characterisation of wood biomass fly ash (WBA-F): a) particle (volume)-size distribution of WBA-F samples and cement, b) XRD analysis of WBA-F (Cc – calcium carbonate $CaCO_3$; Q – quartz Si_2O, C – calcium oxide CaO; M – periclase MgO; F – fairchildite $K_2Ca(CO_3)_2$; Ar – arcanite K_2SO_4; P – portlandite $(Ca(OH)_2)$ [42]

2.3. Matching available raw materials with alternative binders

The overview given in Table 1 provides the starting point for identification of currently available suitable waste materials and their estimated quantitates generated each year. Next step in ensuring feasibility of using certain raw material on industrial scale is connecting relative quantity with possible use in different alternative binders. Table 2 shows this connection between availability of raw materials and their possibility of use. It is clear from this table that in the Southeast European region fly ash, copper slag and blast furnace slag are currently available in significant quantities and can be at the same time used in different applications. Slags will continue to be available in the future, since the production of steel and copper in the region is successfully running. Availability of fly ash could in the future be limited, due to the European announcements of coal phase-out in the electricity sectors [41]. Red mud is available in very significant quantities and the application of this material should attain more attention in the region, especially looking at the versatile possibilities of usage for this material. Finally, limestone and clays are available in abundant quantities in the region and surely present combination which will in future attain higher share of the alternative binders' market.

3. Challenges

3.1. Moving beyond 10 % of cement replacement – the importance of understanding microstructure

Many alternatives can be used as an addition or substitution of cement for up to 5 - 10 %, albeit with limited or insignificant influence on concrete properties. However, proper understanding of mechanisms that trigger and control raw material reactivity is of paramount importance for increasing the replacement levels and reaching more significant ecological benefits [9]. It is only by full understanding of pozzolanic reactivity, hydration reaction and type and properties of phases formed during the reaction that we can modify and control in a desirable way the substitution of cement, and reach high or total cement replacement. Because of the relatively limited combination of chemical compositions, it is possible to develop generic approaches to screening these materials and evaluating their potential for use as SCMs. Thus, a more rapid and significant leap in knowledge and full-scale application in practice can be obtained. A first step in applying generic approach to the replacement of cement is definitely a detailed chemical and physical characterization of raw materials. An example of such characterization is shown in Figure 6.a and 6.b, showing particle size distribution and mineralogical composition, respectively, of different types of wood ash. This characterisation was made within the research project "Transformation of ash from wood biomass into resilient construction composites, TAREC[2]", funded by the Croatian Science Foundation.

Based on detailed characterization of raw materials a preliminary ranking can be made, which could help researchers to focus further search for potentially reactive raw materials on the most promising candidates. Examples of such ranking can be found in paper by Carević, I. et al. [42].

3.2. Application despite the standards - the importance of equivalent performance concept

Currently, the only standardized procedure for designing concrete mixes to meet environmental exposure requirements is a prescriptive provision given in EN 206. The deficiency of the prescriptive durability design approach is that durability properties are specified based on requirements for constitutive materials, construction and curing, without prescribing the exact property, testing method and limiting values for specific material properties. No calculation procedure is defined if longer service life is required for example in the case of infrastructures with the requested service life of over 100 years. Compliance procedure for on-site concrete is merely based on the assessment of compressive strength, since it is almost impossible to effectively control most of the prescribed limiting values. But even more problematic issue is the fact that

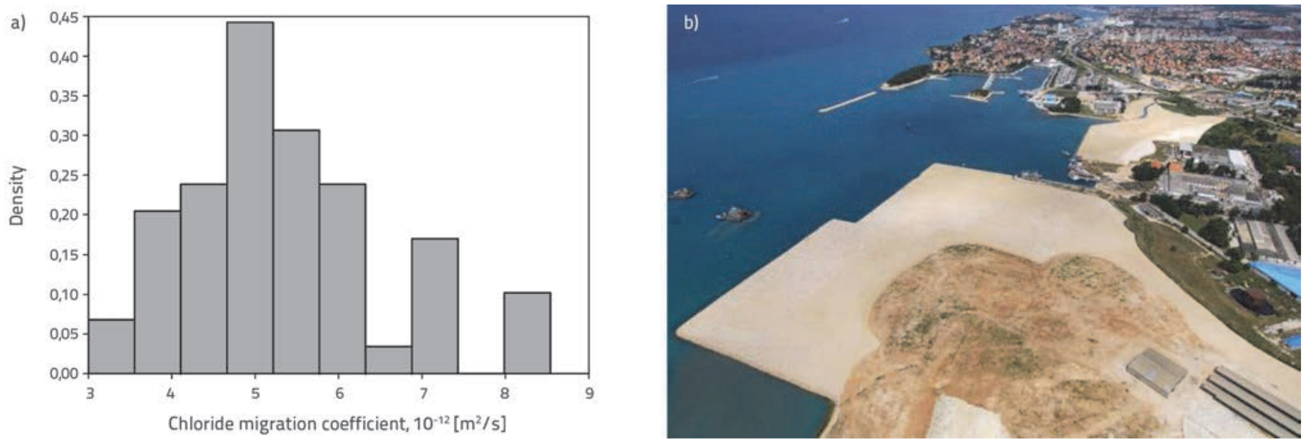

Figure 7. a) Histogram of achieved chloride migration values obtained for a set of concrete samples taken in the scope of the concrete compliance checking procedure during construction of the New Port of Gaženica [45], b) The New Port of Gaženica during construction, with the city of Zadar in the background

the prescriptive approach ignores the different performance of different cement types. It cannot therefore be used for new materials, e.g. alternative binders for concrete.

On the contrary, performance-based design is based on durability indicators, which are properties of concrete that can be proven in the laboratory and on-site and, therefore, can be used during construction as a part of quality control and on-site compliance control [43, 44]. Durability indicators were specified in the New Port of Gaženica project and these durability indicators were continuously checked for compliance during the construction of the port [45]. Example in Figure 7.a shows statistical distribution of chloride migration coefficient values obtained on 53 samples prepared during concreting of reinforced concrete elements. On this project, prescribed chloride migration coefficient values for these elements were in the range of 5-10 10^{-12} m^2/s. The figure also shows that the achieved concrete quality is well within the range of prescribed values, and so it can be concluded that the achieved concrete penetrability property complies with the required concrete penetrability property.

Using performance-based design of concrete structures, instead of merely prescriptive provisions, it would be possible to apply in practice higher substitution of cement with different alternative materials. A step towards this is what is known as the Equivalent Concrete Performance Concept (ECPC) [46]. The ECPC allows amendments to the requirements for minimum cement content and maximum w/c-ratio when a combination of a specific addition and a specific cement source is used. It shall be proven that the concrete has an equivalent performance especially with respect to its interaction with the environment and to its durability when compared with a reference concrete in accordance with the requirements for the relevant exposure class. For ECPC to be established in the practice, methods to test durability of concrete should be standardised and some property values expected for different environment exposure classes established, which is for now not fully implemented even on European level for the traditional OPC concrete. Additionally, for the ECPC to work for different alternative binders, it is necessary to ensure that the testing methods, well-established for OPC concrete, deliver realistic results for alternative binders, and, furthermore, that they can be used, with a certain level of confidence, to judge performance of these materials in real aggressive environments.

3.3. Long-term durability – how sustainable are alternative binders?

Alternative binders have various physical (pore structure, tortuosity of pores) and chemical (pH of pore solution, composition of hydration products) characteristics compared to ordinary Portland cement. It is therefore a question whether physical and chemical degradation models well-established for OPC can explain microstructural changes of ABCs during exposure in aggressive environment.

A perfect example for this is the carbonation of concrete prepared with ABCs. Carbonation is known to affect the durability of cement-based materials under long-term conditions, since it leads to loss of concrete alkalinity and, subsequently, to an increased susceptibility to reinforcement corrosion in OPC-based concrete. In OPC concrete carbonation mainly causes decalcification of portlandite, and if a sufficient portlandite content is available, the properties of concrete are not strongly affected by carbonation. Conversely, in systems containing little or no portlandite carbonation induces decalcification of other hydration products, leading to chemo-mechanical changes inside the concrete, and therefore can affect its porosity, transport and mechanical properties and corrosion of steel [47]. The example given in Figure 8 shows changes of corrosion parameters of steel in non-carbonated concrete after 28 days of curing (Figure 8 a) and in carbonated concrete after 1 month of carbonation (Figure 8b), clearly showing the change of corrosion behaviour in low pH binders after carbonation.

Unlike OPC, the experience with alternative binders does not cover the period of more than 50 last years, and their long-

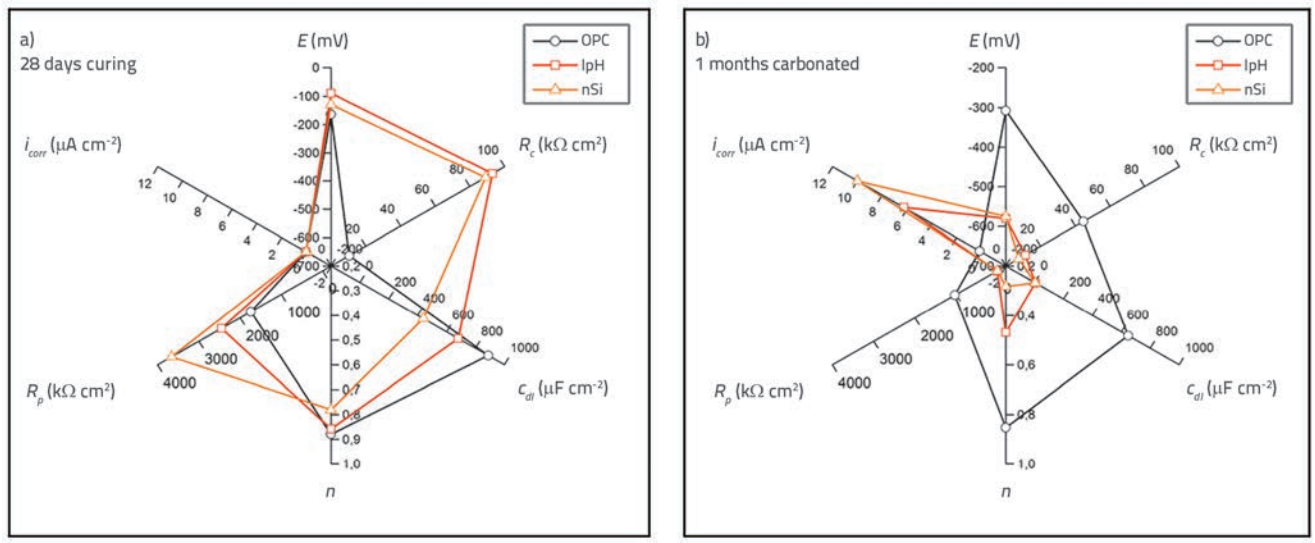

Figure 8. Overview of all corrosion parameters of steel embedded in three different mortars after: a) 28 days curing, b) at the end of the testing period on samples carbonated for 1 month [47]

Figure 9. Test site with exposed concrete columns under Krk Bridge, where different type of stainless steels have been exposed to real marine environment during last 10 years [48]

term behaviour in environment cannot be judged based on exhaustive field tests. It has therefore become obvious that, in order to have some knowledge about their expected behaviour in environment, it is crucial to understand their degradation from nano- and microscopic scale, but also prove their behaviour in real scale exposure sites and using simulation models. Example of established exposure site under Krk Bridge is shown in Figure 9, which was used to evaluate long-term resistance to corrosion of different types of stainless steel. Similar approach should be adopted to alternative materials, in order to follow their behaviour in real environments. In ongoing projects, it will be done with different concrete which include various alternative binders, in order to follow their behaviour in real environments.

4. Research outlook

Various developed binders have distinct chemical and physical properties compared to OPC, which leads to their specific challenges. Some of these challenges for each of the binder mentioned in the paper (high-volume supplementary cementitious materials, SCM; limestone calcined clay, LCC; alkali-activated materials, AAM, calcium-sulfoaluminate cement, CSA) are presented in the Table 3. Specific challenges are grouped in three categories: i) challenges connected to the composition, which are tackled mainly using microstructural analysis as a tool, ii) challenges connected to the practical application of specific binder, which are mainly barriers for market penetration or specific application issues resulting from binder macro properties and iii) challenges connected to long-term sustainability, which are tackled by performing durability studies. For each specific challenge highlighted in the Table 3, references are recommended for further reading for interested readers. Jointly, all recommended studies present an overview

Table 3. Specific scientific challenges for different alternative binders

Type of binder	CHALLENGES		
	Composition	**Practical application**	**Long-term durability**
SCM	- understand synergetic influence of different raw materials when mixed together in a binder [49] - understand pozzolanic / hydraulic reactivity of different raw materials [9] - develop / verify / standardise methods for assessing pozzolanic / hydraulic / chemical reactivity [50]	- resolve legislative issues for import / export and transport of raw materials designated as waste [51, 52] - account for unstable quality of raw materials [53] - provide stable quantity of available raw materials [54]	- investigate influence of carbonation on pore structure and penetrability [55] - investigate resistance to cold climates (freezing / thawing) [56]
LCC	- understand influence of limestone beyond "filler effect" [57] - unlock the potential of clays with different kaolinite content, which are available across the world [58]	- perform life cycle analysis to compare with competing brick / cement industry [59, 60]	- understand reasons for reported improvements of penetrability properties [61]
AAM	- lower the quantity of activators needed [62, 63] - pinpoint alternative (waste) materials for activators [64, 65] - develop hybrid cement-alkali binders [66]	- resolve regulatory and safety barriers for market uptake [67] - verify existent or develop new standards for durability testing [68]	- investigate efflorescence / leaching [69] - investigate influence of corrosion of steel (passivity, initiation and propagation of corrosion) [70]
CSA	- pinpoint sources of bauxite available in abundant quantities [71] - optimise clinkers with specific mineral compositions and engineering properties [72] - understand influence of mineral additions [73]	- account for very fast setting, which is of benefit to some specific applications, but also involves some limitations (e.g. transport, concreting higher quantities, pumping) [74]	- investigate long-term deformation [75] - investigate implications of high porosity and different pore structure on penetrability [76]

of the current research efforts in the field of alternative binders for concrete.

To solve challenges highlighted in the table a coordination and synergy between different research groups is of paramount importance. Some of these challenges will be dealt with in the following years through projects currently undertaken at the Department of Materials, Faculty of Civil Engineering, University of Zagreb, which are funded though national, Swiss and European funds. This includes establishment of a research group and laboratory for an advanced research of sustainable materials.

5. Conclusion

The overview presented in this paper clearly shows that there are certain opportunities for the development of alternative concrete binders in the region. Currently there are numerous types of raw materials and by-products that are being considered as supplementary cementitious materials. At the same time there are several different types of binders developed, which have different composition and macro-scale properties. This is leading to a range of possible solutions when it comes to societal challenge of lowering ecological impact of concrete industry. However, for a more significant application of alternative binders in the practice, several challenges must be considered in a more systematic and coordinated way. Among main challenges recognised in this paper are: importance of microstructural analysis for higher cement replacement levels, importance of applying performance-based approaches to designing concrete durability and importance of durability analysis of alternative materials for ensuring their long-term sustainability. These challenges are jointly providing numerous research perspectives in forthcoming period for researchers in the region and beyond. However, the only way to tackle these challenges and respond to the research needs in an efficient and sustainable way is with a coordination and synergy between different research groups.

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