Implementation of natural and artificial materials in Portland cement

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REVIEW

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Abstract

For the preparation of modern cement and concrete, supplementary cementitious materials (SCM) have become essential ingredients. The technical, economic and environmental advantages of using SCM have become unquestionable. The main technical reasons for their use are the improvement of the workability of fresh concrete and durability of hardened concrete. Actually, SCM affect almost all concrete properties, while environmental and economic reasons may be more significant than technical reasons. These ingredients can reduce the amount of Portland cement used in cement composites, resulting in economic and environmental benefits. In addition, many of the SCM are industrial by-products, which can otherwise be considered as waste. This paper presents a literature review of the present knowledge on the impact of natural zeolite, waste construction brick and waste container glass on physical, chemical and mechanical properties of Portland cement as the most commonly used cement in the world.

Keywords: waste materials, natural zeolite, waste construction brick, waste container glass, heat of hydration

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1. INTRODUCTION

The cement industry plays a very important role in the global economy, especially that of Portland cement as the most used building material [1]. The great advantage of cement lies in its excellent physical, chemical and mechanical properties. Total cement consumption in 2015 amounted to 4.3 billion tons with the total value of 335,000 million US$. The Portland Cement Association (PCA) showed a growth of 3.5 % over the period 2017-2018 [3]. Unfortunately, in the last hundred years the cement industry has had a major impact on the environment. Furthermore, since large amounts of raw materials are needed during the clinker production process to produce billions of tons of cement worldwide, large quantities of CO_2 are also released. Cement industry is responsible for 8 % of CO_2 emissions worldwide [4]. It has been shown that approximately one ton of CO_2 is released in the atmosphere during the production of one ton of Portland cement [5]. Furthermore, during the production of Portland cement and concrete, it is necessary to consume a large amount of energy and natural aggregates, which further loads the ecosystem around us. Globally, the price of energy is growing steadily from day to day as sources of fossil fuels are being exhausted. This leaves an indelible mark on the cement industry and the price of cement. Green taxes are also an additional cost and it is estimated that the price of cement production will be doubled by the year 2030 [6]. In addition, waste from demolition of buildings and the growing need for fillers as additives to cement irreversibly affect the environment and represent concrete as a material that affects negatively sustainable development of the society at large [7].

Previous research has focused on finding alternative materials that can be used as a substitute for cement, such as available and less valuable wastes from industry and agriculture, which potential for use as supplementary cementitious materials (SCM) increases with recycling, recovery and reuse processes. In this regard, researchers investigated the efficacy and possibility of using waste pozzolanic materials [8-11]. These waste materials are secondary products from industrial processes with high silicon and aluminum contents [12]. In the past, numerous tests have been carried out

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using fly ash, blast furnace slag and silica fume as SCM in cement industry. The purpose of this paper is a detailed and clear presentation of zeolite as a natural material as well as waste materials from different industrial sectors that are investigated successfully for use as SCM in Portland cement. Also, we will overview concrete obtained from industrial by-products, non-impact environmental concrete and green building materials. The use of these SCM in cement composites will provide opportunities for use of other industrial wastes for various purposes in the construction industry. Also, in such a way, the cement industry will contribute to the sustainable development of the society.

2. SUPPLEMENTARY CEMENTITIOUS MATERIALS

Today, a large amount of waste materials originates in the world as by-products in various sectors, such as: industry, construction, and agriculture as well as the waste from everyday life [13-18]. Waste can be dangerous if it is not properly disposed [19-22]. By increasing the population, the quantity and type of waste produced increases [23]. These wastes are accumulated in the environment for a long time as unused materials. The solution to this problem lies in the fact that waste materials can be used to obtain a whole range of useful products. New research is being carried out to find new ways for waste utilization. Waste materials and by-products, such as: fly ash, ground blast furnace slag, silica fume, rice husk ash, and waste palm oil ash have been used as additives in concrete for many years [24-30]. Partial or complete substitution of Portland cement with waste materials contributed to alleviation of the landfill problem, reduction of construction materials costs, reduction of the energy use and to protection of the environment.

Today, SCM have a wide range of applications such as pozzolanic materials, which increase the strength of concrete due to the pozzolanic reaction, reduce porosity and improve the durability of concrete [31]. It is a well-known fact that pozzolanic materials contribute to the strength in two ways: by acting as a filler and by carrying out the pozzolanic reaction. The pozzolans are made of reactive SiO_2, which, when mixed with calcium hydroxide, affects the hydraulic properties of pozzolan depending on the composition of the individual components in the pozzolanic material. In such a way, cement with high late strength can be obtained. In essence, the pozzolanic reaction is a simple reaction between $Ca(OH)_2$ (portlandite) and amorphous SiO_2 and can be represented by the expression 1:

$$Ca(OH)_2 + SiO_2 + 2\ H_2O \rightarrow CaH_2SiO_4 \cdot 2\ H_2O \tag{1}$$

An analytic pozzolanic reaction occurs also in cement composites with the addition of any mineral additive (silica fume, fly ash), *i.e.* a substance containing reactive SiO_2 [32]. The pozzolanic reaction removes free $Ca(OH)_2$ in the hydrated cement matrix, delaying the establishment of a chemical reaction equilibrium, or enhancing the hydration of alite and belite. The resulting calcium-silicate-hydrates fill the remaining space in the cement composite, which changes the structure of the pore system; the proportion of smaller pores increases, *i.e.* the pore discontinuity is increased, resulting in reduction in permeability of the cement matrix. The second action is related to the effects of small particles of the pozzolanic material during early hydration when they act as a chemically inert filler. These small particles are most often spherical glass particles, which are considerably smaller than the cement particles, able to fill the internal structure of the cement matrix as a microfiller [33, 34]. Also, they can act as nucleation sites at which hydration products are deposited, thus accelerating the cement hydration. Calcium-silicate-hydrates have a lower density than those of portlandite and pure SiO_2, which results in expansion of hydration products. This process occurs during the hydration reaction between the alkali from the cement and poorly crystalline silicate aggregates [35]. Due to increased greenhouse gas emissions during cement production, the use of SCM in concrete is increasing, whether it is in mixed cements or the additives are added separately during application. These additives can be natural and artificial. The use of SCM without any previous processing significantly reduces CO_2 emissions in the atmosphere. These additives, also called mineral additives or pozzolans, do not possess hydraulic properties but combined with cement these properties are generated. Division of pozzolans into certain categories is not simple. According to one proposition that applies to mineral supplements only, five groups are classified with respect to the chemical reaction type in which these additives participate during hydration as follows [36].

1. Additives potentially exhibiting hydraulic properties for which an activator (*e.g.* sulfate) is needed. This group includes fast-cooled blast furnace slag.

2. Additives with partial hydraulic properties, but also pozzolanic properties. This group includes fly ashes with high contents of CaO >10 % by weight.
3. Additives with high pozzolanic activity. This group includes filter SiO_2 dust from ferrosilicon production or silica fume and rice husk ash.
4. Additives classified as natural pozzolans.
5. Different mineral additives, such as slow-cooled slag and poorly reactive rice husk ash.

The main impacts of the use of pozzolanic materials in cement and concrete are: reduction of the cement content in cement composites, which contributes to lowering costs, reducing heat of hydration, improving the workability of cement composites, achieving projected strength after 28 days of hydration and improving resistance of the cement composite to sulfate action [37-39].

2. 1. NATURAL ZEOLITE AS A SCM

Natural zeolites are a kind of natural pozzolans that has been widely used in construction since ancient times. Natural pozzolans in general largely differ regarding chemical composition, but silicon, aluminum and iron oxides prevail. According to most standards, if a pozzolan contains silica, aluminum and iron oxide amounts above 70 % by weight, it is regarded suitable for use in cement and concrete [40]. Natural zeolites are microporous crystalline hydrated aluminosilicates accommodating alkaline earth metal cations. The zeolite structure consists of a three-dimensional network of $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ tetrahedra connected by oxygen atoms [41]. Neutralization of the negative charge in $(AlO_4)^{5-}$ tetrahedra is achieved by incorporating highly mobile hydrated alkali and alkaline earth cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) in cavities and channels in the zeolite structure. The existence of cavities interconnected by channels of a particular shape and size is the main structural feature that distinguishes zeolites from other aluminosilicates and other crystalline materials. The geometry of free space in dehydrated zeolites is important in determining physical and chemical properties [42-47]. The chemical composition and the XRD image of clinoptilolite as one of the most abundant and used natural zeolites are shown in Table 1 and Figure 1, respectively [48,49].

Table 1. Chemical composition of natural zeolite from Donje Jesenje, Croatia (reprinted from [48] (Barbir D, Dabić P, Lisica A. Effects of mud from a zinc-plating plant and zeolite saturated with zinc on portland cement hydration and properties of hardened cement pastes. Chem. Biochem. Engin. Quartely. 2016; 30(4): 401-409) according to the publisher instructions)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
Content, wt. %	64.93	13.66	2.03	2.99	1.10	1.88	3.66

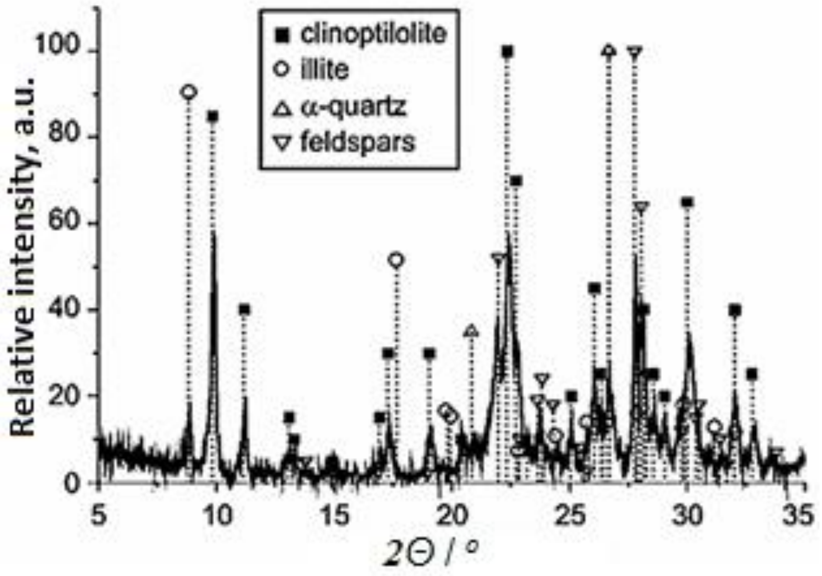

Figure 1. XRD of natural zeolite from Donje Jesenje, Croatia (reprinted from [49] (Rožić M, Cerjan-Stefanović Š, Kurajica S, Rožmarić Mačefatik M, Margeta K, Farkaš A. Decationization and dealumination of clinoptilolite tuff and ammonium exchange on acid-modified tuff. J. Colloid Inter. Sci. 2005; 284(1): 48-56) with permission from Elsevier)

Natural zeolites are the most commonly used natural materials as SCM for cement [50,51]. In China, it is estimated that the total amount of natural zeolite used for this purpose exceeds 30 Mt per year [52]. However, concrete with zeolites is poorly investigated, as opposed to concrete supplemented with silica fume, metakaoline, fly ash and blast furnace slag.

2. 1. 1. POZZOLANIC ACTIVITY OF NATURAL ZEOLITE

Despite the crystal structure, natural zeolites exhibit pozzolanic activity due to their high specific surface and metastability, but the activity also depends on the chemical and mineralogical composition. The pozzolanic reaction of zeolite occurs in the presence of calcium hydroxide released during cement hydration. In a high pH solution, hydroxide ions attack the zeolite structure and decompose the aluminosilicate framework. The resulting ions are released into the solution and react with calcium ions to produce calcium-silicate-hydrates (C-S-H phase) and calcium-aluminate-hydrates (C-A-H phases). C-S-H and C-A-H phases contribute to improved hardened concrete microstructure due to filling of pores, increasing durability and final strength of concrete [53,54]. Also, the influence of natural zeolite on concrete properties was compared with the influence of other pozzolanic materials. In one study it was demonstrated that the reactivity of natural zeolite is higher than the reactivity of fly ash, but lower than that of silica fume [55]. Previous work investigating natural pozzolans primarily zeolites showed that zeolite tuffs exhibited excellent pozzolanic activity being more reactive than glass-based materials with respect to lime fixation [56-58]. Also, pozzolanic activity of synthetic zeolites was investigated concluding that a zeolite with a lower content of silicon is more reactive, while a zeolite with higher silicon contents contributes to higher cement strengths [59]. However, more research is needed to fully explain the reasons for the greater pozzolanic activity of zeolite minerals compared to that of the other natural aluminosilicate materials.

2. 1. 2. HEAT OF HYDRATION WITH ADDITION OF NATURAL ZEOLITE

Calorimetry at the constant temperature allows accurate measurement of developed heat per unit of time. Since the influence of external temperature on the working conditions of the calorimeter has been excluded, it is possible to ease determine all exothermic reactions occurring during hydration of a fresh cement paste. There are two exothermic peaks on the calorimetric curve (Figure 2). The first peak occurs after a few minutes of hydration with a very pronounced intensity in a short period of time, which corresponds to the initial moistening of the sample, dissolution and to reactions of the aluminate phase C_3A (tricalcium aluminate) with sulfates from gypsum (binding regulator). As a result of these reactions the main crystalline product, ettringite ($3CaO\ Al_2O_3\ 3CaSO_4\ 32H_2O$) is formed. Also, amorphous compounds having the AFt (calcium aluminate trisulfate-ettringite phase) phase are formed. A hydrate layer around C_3A particles is created, causing the hydration reaction to slow down [60,61]. According to Costoya, during the initial period, a portion of C_3S (alite) is also reacted [62]. By adding zeolite, the content of reactive aluminum in the cement system increases. This may be reflected in the intensity of the first peak. Namely, the intensity decreases as the zeolite amount increases, as can be seen in Figure 3 [63]. In this case, effects of nucleation on the smallest zeolite particles cannot be neglected. However, the smallest zeolite particles are larger than the Portland cement particles. After the initial period the hydration reaction is slowing down termed as the induction period, which provides information on the workability time. The heat value drops sharply and remains constant for several hours. In the induction period, the concentration of Ca^{2+} ions reaches saturation with respect to $Ca(OH)_2$.

The main peak of heat released occurs due to nucleation and growth of the C-S-H phase and $Ca(OH)_2$. Mechanisms that explain the beginning of the acceleration period of hydration are still not compliant. Some researchers pointed out that the hydration rate in this period depends primarily on the amount of C-S-H products [64,65]. The starting point of the hydration acceleration period corresponds to the beginning of binding, while the second peak indicates the end of binding and the beginning of solidification of the cement paste. Addition of natural zeolite to the cement-water system does not affect the beginning of the acceleration period and the main peak appearance but it affects the main peak intensity (by increasing the additive amount there is a decrease in the heat release rate), as can be seen in Figure 3.

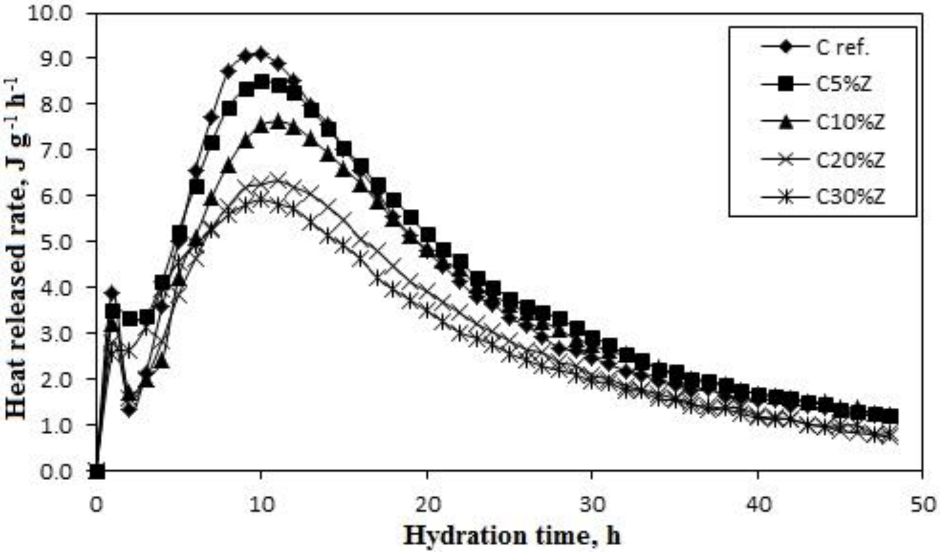

Fig. 2. Heat released rate of samples Portland cement with addition of natural zeolite from Donje Jesenje, Croatia (C ref. - ordinary Portland cement, C5 %Z, C10 %Z, C20 %Z and C30 %Z – sample Portland cement with addition of 5, 10, 20 and 30 mas. % of natural zeolite (reprinted from [63] Barbir D. Studija utjecaja štetnih otpada na procese hidratacije i fizikalno-kemijska te mehanička svojstva cementnih kompozita. PhD Thesis. Split: Kemijsko-tehnološki fakultet; 2013)

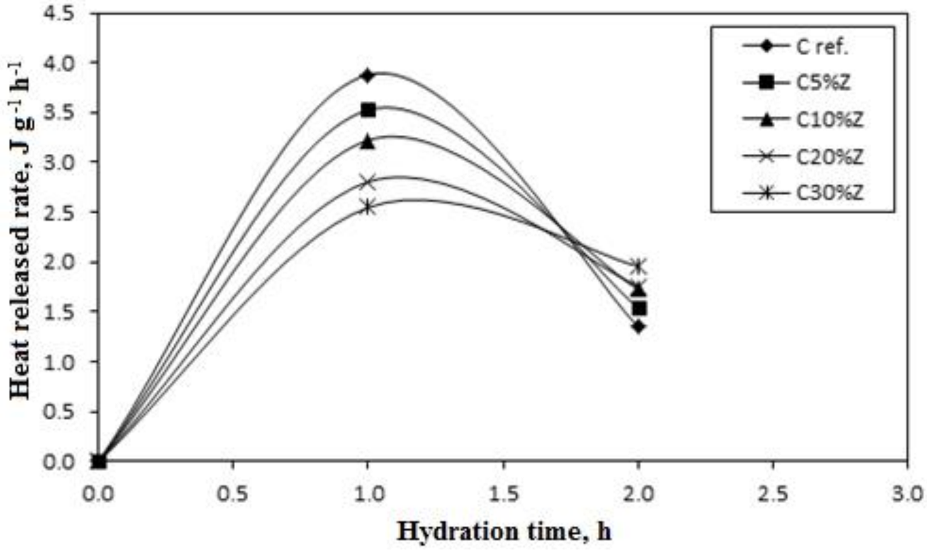

Fig. 3. The first peak of the heat release rate of Portland cement with the addition of natural zeolite from Donje Jesenje, Croatia (C ref. - ordinary Portland cement, C5 %Z, C10 %Z, C20 %Z and C30 %Z – sample Portland cement with addition of 5, 10, 20 and 30 mas. % of natural zeolite (reprinted from [63] Barbir D. Studija utjecaja štetnih otpada na procese hidratacije i fizikalno-kemijska te mehanička svojstva cementnih kompozita. PhD Thesis. Split: Kemijsko-tehnološki fakultet; 2013.)

Zeolite addition affects adsorption of Ca^{2+} ions on the surface of the pozzolan either as a surface layer or in the form of a C-S-H phase at the beginning of the hydration acceleration period. According to Richardson, this mechanism will enable even faster dissolution of C_3S grains contained within a thin and porous layer of the C-S-H phase [66]. The acceleration period is followed by a deceleration period of hydration and diffusion. This period is characterized by a small amount of developed heat and is controlled by diffusion of ionic species and by deposition of products in a system which porosity has been reduced.

Values of total released hydration heat are very similar to all cement samples with zeolite after the first 10 h of hydration (Figure 4) [63]. Similar behavior was noted by Tydlitát *et al.* for early-stage hydration heat development in blended Portland cement containing natural zeolite in an amount of up to 40 % by mass [67]. On the other hand, a significant decrease in developed heat after the second peak in the hydration deceleration period was observed with addition of natural zeolite [63]. As can be seen in Figure 3, zeolite had the same effect on developed heat curves, both in the acceleration period, as well as in the period of deceleration and diffusion.

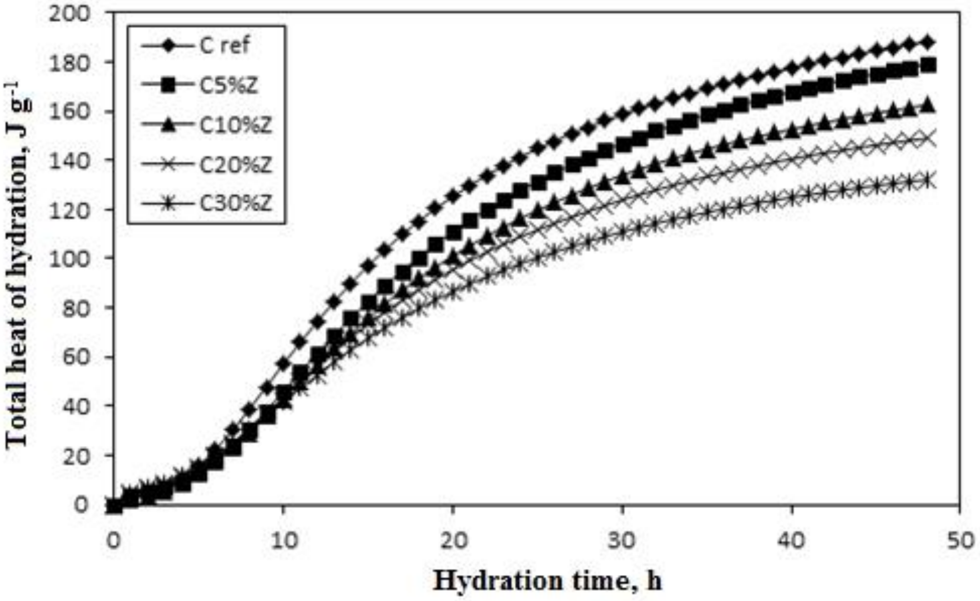

Fig. 4. Total released heat of hydration after 2 days for cement samples with addition of natural zeolite from Donje Jesenje, Croatia (C ref. - ordinary Portland cement, C5 %Z, C10 %Z, C20 %Z and C30 %Z – sample Portland cement with addition of 5, 10, 20 and 30 mas. % of natural zeolite (reprinted from [63] Barbir D. Studija utjecaja štetnih otpada na procese hidratacije i fizikalno-kemijska te mehanička svojstva cementnih kompozita. PhD Thesis. Split: Kemijsko-tehnološki fakultet; 2013)

2. 1. 3. DEVELOPMENT OF COMPRESSIVE STRENGTH WITH NATURAL ZEOLITE ADDITION

Compressive strength is the ability of a material to withstand axially directed pressing forces. Over the years, numerous studies have been carried out on the effects of natural zeolites on development of the compressive strength of cement mortars and concrete. However, it is still difficult to estimate the influence of zeolite as a SCM on cementitious and concrete properties, especially on the development of compressive strength. Many factors influence the strength and durability of the composite, such as: the water/cement ratio (W/C), the SCM content, the mineral and chemical composition of the zeolite, the particle size, the zeolite purity, and the pozzolanic activity [68,69]. The use of natural zeolite in mixed Portland cements leads to an increase in water requirements and a decrease in the rate of strength development of the cementitious systems. Poon et al. investigated the influence of various W/C ratios on the properties of mixed cements with the addition of zeolites and they concluded that in blended cement pastes with a lower W/C ratio, the natural zeolite contributes more to the strength of the pastes. But in the pastes with a higher W/C ratio and a lower cement replacement level it undergoes a higher degree of reaction [51]. In another study it was shown that the strength of the concrete decreased with the addition of zeolite at a W/C ratio over 0.45 [55,70]. On the contrary, Ahmadi and Shekarchi found that concrete with added zeolite at W/C=0.40 had higher compressive strength than the reference sample after 3, 7, 28 and 90 days of hydration [68]. Addition of zeolite from western Texas to concrete at a W/C=0.48 decreased the compressive strength after 56 days of curing while after 90 days the compressive strength was greater than that of the reference sample without the zeolite [71]. Several previous studies have investigated the impact of different contents of natural zeolite on the development of compressive strength [55,68,71,72]. Partial replacement of cement with 15 and 25 wt.% of natural zeolite did not affect the increase in strength after 28 days of hydration. After 90 days, samples with 25 wt.% of fly ash had greater strengths than the samples with addition of 15 and 25 wt.% of natural zeolite and a reference sample without additives. Based on the results obtained, Shon and Kim concluded that for concrete, the optimal replacement of cement with natural zeolite is in the amount of 20 % [71]. In another study, replacement of Portland cement by 15 wt.% with natural zeolite, induced an increase in the concrete strength for 14 % after 28 days of hydration [55]. Similarly, the compressive strengths of concrete with 5, 10, 15 and 20 wt.% of natural zeolites were higher than that of the Portland cement sample without a zeolite for that of 14, 16, 23 and 25 %, respectively. In addition, compressive strength results after 90 days of hydration showed that the optimal zeolite content was 15 wt.% [68]. Conpolat et al. investigated the effects of natural zeolite and fly ash as SCM on Portland cement properties. According to their results, it is possible to obtain satisfactory compressive strengths by 20 wt.% substitution of cement with zeolite and addition of 5 wt.% zeolite + 5 wt.% fly ash [72].

2. 2. WASTE CONSTRUCTION BRICK AS A SCM

Construction and demolition waste (CDW) is the waste that has the highest volume and weight of all waste generated in the EU. In developed countries, hundreds of Mt of CDW are produced annually. The EU generates over 100 Mt per year, while according to EPA, the US generates 136 Mt of CDW per year [73,74]. CDW represents 25-30 % of all waste generated in the EU and consists of several materials, such as: concrete, bricks, gypsum, wood, metals, plastics, solvents, asbestos and excavated land. CDW arises from building of construction objects and roads, but also during maintenance. CDW has been awarded a priority label for the EU in terms of reducing its volume. As most of these materials can be recycled, there is a great potential for recycling and reuse of CDW, since some components are valuable raw materials. Namely, there is a whole market for the reuse of CDW as road aggregates, drainage systems and other construction applications. Technology of recycling and separating various types of CDW is well known, easily accessible and generally inexpensive [75].

In the total amount of CDW, products of calcined clay, especially brick, are about 30-80 %. Today, the recycled brick is used as an aggregate, for picking tennis courts and as a herbal substrate. In civil engineering, it can be used in unrelated systems such as drainage layers, road layers or dam construction material. On the other hand, it is also possible to use it in concrete and asphalt [76].

Investigations on the use of ground bricks as fine additives to cement are relatively new. Not very frequent use of this additive stems from an unusually high water absorption, which can adversely affect the properties of the cement composite (especially on the compressive strength).

The average chemical composition of waste construction brick is shown in Table 2. [77]

Table 2 Chemical composition of waste construction brick (reprinted from [77] Barbir D, Dabić P, Lisica A, Barbir D. Recycling and reuse of waste building brick in cement composites. In Šolić S, Šnajdar Musa M. eds. Conference Proceedings: International Conference on Materials MATRIB 2014, Vela Luka, Croatia: Croatian Society for Materials and tribology; 2014: 30-39).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O
Content, wt. %	63.42	15.36	6.18	6.60	2.99	3.03

It can be noticed that ground construction brick contains a large amount of silicon and aluminum oxide (over 70 %), which makes it potentially a good SCM due to its pozzolanic properties.

2. 2. 1. POZZOLANIC ACTIVITY OF WASTE CONSTRUCTION BRICK

Clay in the natural state does not exhibit pozzolanic activity, but during the calcination process, the pozzolanic reaction with lime in the presence of water is enabled. The structure of clay minerals breaks down at 600-950 °C, allowing a chemical reaction with calcium hydroxide. However, in clay mixes with large amounts of highly crystalline minerals, such as quartz and feldspar, it is not possible to obtain satisfactory pozzolanic activity [78]. During calcination, bonded water from clay is lost, causing decomposition of the crystalline aluminosilicate structure to produce amorphous compounds of aluminum and silicon. Aluminum and silicon in the amorphous state have a potential to bind with calcium hydroxide. However, if the calcination temperature exceeds 950 °C, silicon and aluminum will pass from the amorphous to the crystal state and form stable compounds such as mullite, which does not react with lime [79]. During the transition to the amorphous state dehydration takes place, so that 10-15 % weight loss occurs due to water evaporation. This transition takes place at different temperatures for different clay types. Studies have shown that the optimal calcination temperature for kaolinite is between 550-950 °C, for Na-montmorillonite 740-920 °C and for illite 650-940 °C. The increase in the amorphous phase can be attributed to increasing the amounts of silicon and aluminium soluble in alkali. Most of calcined clays during the reaction with lime create a variety of reaction products. Which products will originate depends primarily on the chemical composition of clay, while the product amount and type depends on the intensity of the pozzolanic reaction? The main products are C-S-H phases and tetra calcium aluminate hydrates at various concentrations. Also, during the pozzolanic reaction with the calcined clay rich in aluminum, C_2AH_8 and C_3AH_6 phases are formed [80]. Resulting C-S-H phases consist of poorly crystalline foils or tiles with a tobermorite structure. The exact chemical composition of calcium silicate hydrates produced by the pozzolanic reaction varies depending on water/solid ratio and temperature, but also the composition changes during the reaction [81].

2. 2. 2. HEAT OF HYDRATION WITH ADDITION OF WASTE CONSTRUCTION BRICK

The effect of ground brick addition in Portland cement on the developed heat during first two days of hydration is similar as that of natural zeolite addition. The effect of brick on the hydration processes is particularly pronounced during the hydration acceleration period. The control sample without the brick addition had the highest peak on the total developed heat curve, while as brick is added this maximum is retained at a similar position but becomes less pronounced (ref). As Alhozaimy et al. demonstrated, this confirms that the brick addition to Portland cement reduced the heat released during the first 24 h of hydration. This heat reduction can be attributed to the reduced content of the active component (*i.e*. Portland cement) in the system [82]. From this it can be concluded that the ground brick decreases the developed heat in the cement system, which is a very important factor that needs to be considered especially in the production of massive structures and thus opens the possibility of using this material for this purpose.

2. 2. 3. DEVELOPMENT OF COMPRESSIVE STRENGTH WITH THE ADDITION OF WASTE CONSTRUCTION BRICK

In general, concrete supplemented with waste bricks exhibits lower strength than the conventional concrete. This finding can be attributed to greater absorption of water by recycled brick. Reduction in the compressive strength is greater with the increase in the brick content. Debieb and Kenai found that after 28 days of hydration there was a reduction of 10-35 % in compressive strength in the concrete with 25-75 % brick as compared to the non-supplemented concrete [83]. In many studies compressive strengths of concrete with recycled brick addition were determined as 20-40 MPa after 28 days of hydration. However, the strength of concrete with recycled brick depends primarily on the strength of the original brick. For example, the strength of concrete with recycled brick obtained from the initial high strength brick may be greater than the strength of concrete with granite, which is used for production of high strength concrete (UHPC) [84-86]. Generally, it is possible to predict the strength of concrete with the addition of brick as a SCM. This assessment is very important if the recycled brick is used for production of new concrete, which could be optimized regarding the desired strength. Concrete with blown air can be produced very easily with crushed brick. The compressive strength of such concrete is close to the strength of concrete made with a granite filler [87,88].

2. 3. WASTE CONTAINER GLASS AS A SCM

Glass is produced in many forms, such as containers, plate glass (windows and windshield glass), lamps and cathode tubes in TV sets and monitors. All these products have a limited lifetime, after which they have to be recycled to reduce their impact on the environment. Traditionally, container glass was disposed of as a household waste that ended up in landfills, collected at certain recycling sites, or pulled out of the garbage and then transferred to collecting stations. In 2005, about 130 Mt of waste glass emerged per year, of which 33 Mt in the EU, 32 Mt in China and 20 Mt in USA [89]. The main objective of environmental protection institutions is to reduce, as much as possible, disposal of glass after use on landfills and redirect to reuse in order to obtain sustainable viable glass products [90].

Glass is a unique inert material that can be recycled many times without changing the chemical properties. In other words, bottles can be easily broken, melted and converted into new bottles without any significant change in glass properties [91]. Most of the glass produced is in the form of containers for wine, juices and other food products, while if recycled, it is usually re-used to produce that same packaging. Efficiency of this process depends on how glass is collected and sorted in different colors (transparent, green, and brown). However, when glass of different colors is mixed such a mixture becomes unsuitable for producing new packaging and must be used for other purposes or disposed of on landfills [92]. Reindl has demonstrated numerous glass applications such as: road filling aggregates, asphalt production, concrete aggregates, civil engineering (brick and tiles production, wall panels), glass insulation, glass fiber production, fertilizer production in agriculture *etc.* [93]. In this paper, special emphasis is put on the use of glass residues in cement and concrete. Many researchers have pointed out that waste glass has similar chemical composition and phases as traditional SCM and can be therefore easily added to the cement system [94-97].

The main focus on the use of glass in concrete is directed to the chemical reaction between glass particles with silicon and alkali at high contents in the pore solution of cement. This reaction is called alkali-silicate reaction (ASR) and can be very damaging to the stability and durability of the concrete, unless measures are taken to reduce its negative effects. Such preventative actions can be achieved by incorporation of suitable pozzolanic materials such as fly ash, silica fume (SF) or granulated blast furnace slag in appropriate ratios. Glass is very sensitive to alkalis, so glass aggregates or glass fibers can easily engage in the ASR in the concrete, causing adverse effects on the concrete structure. However, fine grained glass (glass powder) is expected to exhibit pozzolan properties such as those of fly ash, natural zeolite and waste brick, thereby preventing the ASR and damage to concrete in the presence of reactive aggregates. This is confirmed by many researchers. For example, fine glass particles in size <75µm were shown to act as a pozzolanic material and prevent the ASR with grain aggregates [98,99]. In another work it was demonstrated that up to 35 % glass content in combination with low-alkali cement can be used in concrete without any adverse effects [100].

2. 3. 1. POZZOLANIC ACTIVITY OF WASTE GLASS

Pozzolanic activity in cement and concrete is most influenced by the pozzolan fineness, chemical composition and composition of the pore solution [101,102]. Shi and associates noted that waste glass became pozzolan active at particle size <300 µm [103]. This size can be achieved by a milling process in a ball mill, which is generally used in the cement industry for grinding cement clinker. When using ground glass or glass powder in cement systems, the glass particle size is not suitable for the ASR but the high alkali content in the glass can cause harmful expansion [104,105]., It was demonstrated by the Chapelle test that lower amount of glass powder is required with higher CaO consumption in the pozzolanic reaction as compared to glass powder with bigger particles, which can be attributed to the larger contact surface. Furthermore, green glass showed better pozzolanic activity than colorless glass [106]. As glass particles were finer, more water was absorbed, which eventually reflected on the mechanical properties of cement composites.

2. 3. 2. HEAT OF HYDRATION WITH THE ADDITION OF WASTE GLASS

The effect of glass powder addition in Portland cement on the developed heat during early hydration is similar as that of natural zeolite and waste brick addition. The released heat curves retain the same shape and show similar behavior in the individual stages of hydration. Dilution or content reduction of the active component (Portland cement) occurs by increasing the content of waste glass powder in the cement system. Therefore, this dilution leads to a lower concentration of Ca^{2+} ions in the cement system [107-109]. Consequently, this results in a delay of Ca^{2+} depletion and prolonging the induction period. Replacement of cement with glass powder to a certain extent, slows down the process of early hydration of the composite cement. Higher glass content leads to a lower heat value and a longer time to reach another exothermic peak. The main factor affecting the heat of hydration is the poor hydration activity of glass powder. Likewise, the total heat released is proportionately reduced by increasing the amount of glass added in the system. On the one hand, the replacement of cement by glass increases the W/C ratio, so there is more space for hydration products. On the other hand, glass powder of sufficient fineness can also act as a nucleation site for hydration products by enhancing nucleation and crystal growth [110-113].

2. 3. 3. DEVELOPMENT OF COMPRESSIVE STRENGTH WITH THE ADDITION OF WASTE GLASS

For many years, researchers have been investigating the impact of waste glass on mechanical properties of concrete [114-118]. In general, the results have shown that aggregates based on waste glass reduce the strength of cement composites. This behavior is attributed to very reactive silicon that can engage in the ASR with alkali in cement paste and lead to expansion and cracking of concrete [119,120]. Glass particles less than 1.18 mm in size were shown to cause lower expansion than fine natural aggregates even after longer testing periods [121]. However, when the waste glass is grounded to a particle size less than 75 µm, concrete samples have achieved a prolonged compressive strength development, which can be attributed to the pozzolanic nature of the very fine glass powder [122]. Partial replacement of cement with glass powder can reduce the strength during early hydration, but it will increase during the later period of hydration. For example, it was found that concrete with 30 wt.% of glass powder with the particle size < 38 µm achieved higher compressive strength after 90 days of hydration as compared to the reference concrete [123]. Also, concrete with 20 wt.% glass powder was shown to exhibit a higher compressive strength only after 28 days of hydration, attributed to the fact that the glass particle size is close to or lower than the particle size of the Portland cement [124]. Similar conclusion came from Khmiri *et al.* [125]. In another study it was shown that the use of glass powder with the particle size up to 10 µm and the content up to 40 wt.% as a SCM can reduce the expansion due to the ASR. However, all samples with glass addition showed lower values of compressive strength [126].

3. CONCLUSIONS

From the results presented in this review paper, the following conclusions can be drawn:

- Natural zeolites are the most commonly used natural materials as SCM. The pozzolanic activity of natural zeolite is influenced by a large specific surface and metastability, as well as the chemical and mineralogical composition of zeolites. Natural zeolites contribute more to the development of compressive strength at a lower water/cement ratio.
- There is a great potential for recycling and reuse of waste construction brick, since some components are valuable raw materials. Investigations on the use of ground brick as fine additives to cement are relatively new. Not very frequent use of brick as a finely ground additive stems from an unusually high water absorption that can adversely affect the properties of the cement composite (especially on the compressive strength).
- Waste glass becomes pozzolan active at particle size <300 µm. Partial replacement of cement with glass can reduce strength during early hydration but will increase during later hydration periods.

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SAŽETAK

Primjena prirodnih i sintetskih materijala u portland cementu

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Dodaci cementu postali su ključni sastojci za pripremu modernog cementa i betona. Često se ne postavlja pitanje o tehničkim, ekonomskim i ekološkim prednostima korišćenja dodataka cementu. Glavni tehnički razlozi za njihovu upotrebu su poboljšanje obradivosti svežeg betona i trajnosti očvrslog betona. Zapravo, dodaci utiču na gotovo sva svojstva betona. Međutim, ekološki i ekonomski razlozi mogu biti značajniji od tehničkih razloga. Ovi sastojci mogu smanjiti količinu portland cementa koji se koristi u cementnim kompozitima, što rezultira ekonomskim i ekološkim koristima. Pored toga, mnogi dodaci cementu su industrijski nusproizvodi, koji se inače mogu smatrati otpadom. Ovaj rad prikazuje pregled dosadašnjih saznanja o uticaju prirodnog zeolita, građevinske opeke i otpadnog stakla na fizička, hemijska i mehanička svojstva portland cementa kao najčešće korišćenog cementa u svetu.

Ključne reči: otpadni materijali, prirodni zeoliti, otpadna građevinska opeka, otpadno ambalažno staklo, toplota hidratacije