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Case study

Evaluation of Industrial by-products as pozzolans: A road map for use in concrete production

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ABSTRACT

The concrete industry is eagerly pursuing the economic advantages of concrete and the improvement of its long-term properties. One of the most effective approaches to improve concrete properties is associated with replacing part of the Portland cement with pozzolanic additives. Although commercial pozzolans like silica fume have proven to be effective, they come at a high cost. Therefore, the modern construction industry is researching pozzolan alternatives. These new pozzolans could come as by-products from different industries, usually accompanied by low-prices, but their efficiency is questionable in most cases. Therefore, fast and reliable evaluation of the materials' efficiency is necessary. This study aims to summarize techniques adapted for evaluation of pozzolanic materials in a roadmap and do evaluation of waste stream pozzolanic materials. Four characterization directions were considered – chemical and physical analysis (i and ii) and direct and indirect pozzolanic activity test methods (iii and iv). Five commercial or waste stream pozzolanic materials were compared and results evaluated. Industrial by-products (glass E, glass K, metakaolin) are studied as alternative pozzolans and compared to silica fume and fly ash. Selected materials are evaluated using testing methods, such as XRF, FTIR, XRD, micro-granulometry, BET, Frattini test, saturated lime test, strength activity index and alkali–silica reaction tests. The evaluation roadmap for pozzolan quality assessment is proposed. Results indicate that commercial material silica fume can meet the requirements followed by the test procedures given in roadmap. Promising result was obtained for E glass which also passed the quality assessment and showed respectable performance results. Rest of materials failed such an important parameter as alkali content. Besides, it was concluded that only complex dissemination provides a trusted result, as the Frattini test and saturated lime test showed promising results, the results do not always match the results of the strength activity index and alkali–silica reaction.

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1. Introduction

According to the Resource Efficiency Roadmap, the building sector is one of the key sectors addressing the challenges of energy, climate change and resource efficiency [1]. The presence of legally binding guidelines in EU legislation regarding waste has already contributed significantly to waste management practices and innovations in the field of recycling; it has also limited the landfilling process and created incentives to change consumer habits. Thus, it is important to focus on the efficient use of resources by replacing commercially-available products with industrial by-products or waste materials. The concrete industry is the largest in the building sector, so the focus of reaching the targets mentioned above is in the daily scope for engineers and researchers. Reducing the costly and environmentally aggressive Portland cement and increasing concrete durability are the targets that act as guidelines for concrete development. Both issues have proven to be partially solved by incorporating supplementary cementitious materials, also known as pozzolans, in concrete composition. Following the American standard ASTM C125, the pozzolans contain siliceous and aluminous materials, which possess little or no cementitious value but will, in finely divided forms in the presence of moisture, react chemically with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties [2]. Pozzolans are usually introduced in the composition of concrete to reduce the amount of cement needed and improve its durability [3–5]. Pozzolans reduce absorption, permeability and ion diffusivity by reducing the porosity of the binder due to the formation of a calcium silicate hydrate gel from the pozzolan and excess $Ca(OH)_2$ coming from the Portland cement. The amount of pozzolans introduced varies, from 5 to 40 wt.% of the cement [6]. The typical natural pozzolans are metakaolin [7], pumice [8] and natural zeolites [9], while the most popular commercial material used as a pozzolan in the concrete industry is silica fume and fly ash [10,11]. Different waste-origin pozzolans are being intensively researched as alternatives to existing ones, and the most promising are calcined clay and glass waste, different types of ashes including coal bottom ash, which could reduce the total cement content by 20 wt.%, retaining the given strength class and also reducing concrete cost by 9% [12–14]. The major concern regarding the use of waste glass as supplementary cementitious materials are alkali content. It is concluded that alkali content within glasses should be limited to a maximum of 4% [13]. This is why in this research two types of glasses were evaluated regarding to its alkali content – low alkali glass (<4%) and high alkali content glass (>4%).

It is well-known that pozzolanic activity mainly depends on the amount of amorphous silica and alumina in the composition of the pozzolanic material [15]. However, it is also affected by other properties such as specific surface area and particle size distribution [16]. One exact and trusted instrumental method that fully evaluates the efficiency of pozzolans is not yet known. X-ray fluorescence (XRF) and X-ray diffraction (XRD) are instrumental test methods that give an initial idea about materials as potential pozzolans by the determination of silica and aluminium oxide in composition (by XRF) and by the determination of the amorphous phase (by XRD). A higher surface area and smaller particle size may ensure more rapid chemical reactions, which are important factors for pozzolans to describe their pozzolanic activity [17], [18]. The pozzolanic activity can be directly assessed by test methods like the Frattini test and saturated lime test. The Frattini test describes the dissolved Ca^{2+} and OH- concentrations in a solution containing saturated lime and the test pozzolan, while the saturated lime test shows the amount of the dissolved Ca^{2+} and OH- concentrations in a solution containing CEM I and the test pozzolan. Alternatively, pozzolan activity can be evaluated indirectly by the strength activity index (SAI) following BS 3892 [19]. In this case, the mortar must maintain 75% of the compressive strength, with 20% of the cement replaced by pozzolans [19].

The aim of this research is the evaluation of industrial by-products through developed evaluation roadmap based and fundamental instrumental investigation methods for fast and reliable evaluation of pozzolans coming from industrial by-products. Thus, three different potential pozzolans – glass E, glass K and metakaolin were studied and compared with a commercially-available pozzolan – silica fume and fly ash.

2. materials and Methods

2.1. Raw materials

Five different high silica and alumina containing materials were studied as pozzolans. The chemical compositions of all solid raw materials used are given in Table 1.

Table 1
Chemical composition of solid raw materials (weight%).

	Al_2O_3	SiO_2	CaO	SO_3	MgO	Fe_2O_3	Na_2O	K_2O	B_2O_3	LOI	Other
CEM	3.9	18.8	63.2	3.3	3.2	3.0	0.2	1.1	0.0	3.0	0.3
SF	0.2	98.4	0.2	0.1	0.0	0.0	0.2	0.2	0.0	0.5	0.2
EG	14.1	52.3	23.4	0.2	0.0	0.4	0.9	0.0	8.5	0.05	0.15
KG	2.8	76.1	0.0	0.0	0.0	0.1	21.0	0.0	0.0	0.05	0
MK	39.6	48.0	0.9	0.1	0.4	0.9	8.9	0.0	0.0	1.0	0.2
FA	27.5	50.8	2.9	0.65	1.3	6.4	0.6	2.2	0.0	1.4	6.25

Silica fume (SF) preparation Elkem Microsilica Grade 971-U (Norway) was used in the of the pastes and mortars as a commercially-available pozzolanic additive, whose chemical composition is given in Table 1. Coarse particles > 45 μm were 0.2%; bulk density was 300 kg/m^3. The specific gravity of the SF was 2.15 g/cm^3. SF was used as the reference pozzolan.

Fly ash (FA) is a commercial material from the coal-fired power plant Ostroleka (Poland). The studied FA is class F, in accordance with the ASTM standard C6128–03.

Glass E (EG) and *glass K (KG)* were taken from the glass fibre factory Valmiera Glass Group JSC (Latvia), where they produce different types of glass products, including glass fibres. This study used the surpluses of glass fibres. Glass fibres approximately 50 mm long were cut and ground in the planetary ball mill Retsch PM 400 with a speed of 300 rpm for 30 minutes to obtain a powdered material.

Metakaolin (MK) was obtained from the porous glass granule production factory Stikloporas UAB (Lithuania). In this case, the metakaolin is a by-product from the final stage of expanded glass granule production, where kaolinite clay powder is used as a substance for anti-agglomeration at 850 °C for 40–50 m. MK is characterised as having a higher alkali content than metakaolin obtained from pure kaolin because, during production, glass powder particles with a high alkali content remain in MK.

The research used CEM I 42.5 N-type *Portland cement (CEM)* made by Cemex Ltd (Latvia) to describe the impact of the chosen pozzolans on cement mortars and for the Frattini test. The specific gravity and fineness (Blaine) of the cement were 3.15 g/cm^3 and 3787 cm^2/g, respectively. The chemical composition of the cement is given in Table 1. The mineral composition of the cement clinker is: C_3S: 57.7%, C_2S: 18.2%, C_3A: 6.4%, C_4AF: 9.8%, CaO_{free}: 2.0% and Na_2Oekv: 0.9%. *Hydrated lime* CL90 *(CL)* provided by Lhoist Poland Ltd (Poland) was used as a Ca^{2+} source for the pozzolan activity test.

Commercially-available *quartz sand* < 4 mm produced by Saulkalne Ltd. (Latvia) was used as fillers for cement mortars.

2.2. Techniques

The particle size distribution in powdered materials was determined by the Analysette 22 NanoTec laser granulometer. The specific surface area and porosity of the pozzolans were studied via nitrogen sorption and desorption based on the Brunauer–Emmett–Teller (BET) theory [20]. The specific surface area was measured using QUADRASORB SI (Quantachrome Instruments, Boynton Beach, USA) equipment. Degassing was performed to remove moisture and other contaminants from the surface of specimens, according to the IUPAC guidelines. The degassing was performed for 24 h at 100 °C using Autosorb Degasser Model AD-9.

The XRD characterisation of studied pozzolans was performed using a BRUKER-AXS D8 ADVANCE X-ray diffractometer, using CuKα1, α2 radiation in the range of 5–70° (2θ).

The Varian 800 FT-IR Scimitar Series spectrometer was used to obtain FTIR spectra in the range from 1600 to 400 cm^{-1} with a resolution of 4 cm^{-1}. Specimens for the FTIR measurements were prepared via mixing 300 mg of KBr with 1 mg of the sample.

The Frattini test described in EN 196-5 was used to describe the pozzolan activity [21]. For each direct pozzolan assessment method three parallel measurements were done and mean value calculated. First, 4 g of respective pozzolan and 16 g of CEM were mixed with 100 ml of distilled water. After eight days, the samples were filtered and cooled to ambient temperature in sealed Buchner funnels. Obtained liquids were analysed for OH- by titration against dilute HCl with a methyl orange indicator and for Ca^{2+} by pH adjustment to 13 [22]. Results are presented as a graph of Ca^{2+}, expressed as equivalent CaO, in mmol on the y-axis versus OH- in mmol on the x-axis. The solubility curve of $Ca(OH)_2$ was plotted to describe the pozzolanic activity: results of samples lying below this curve indicate the removal of Ca^{2+} from the solution – those samples can be assumed as pozzolans. The results of samples lying on the curve are indicative of zero pozzolanic activity, and results above the curve correspond to no pozzolanic activity. At the same time, it is worth noting that this test method does not assume other sources of soluble calcium that might be present in the system, as leaching of calcium would invalidate this approach.

For the saturated lime test, 2 g of hydrated lime were dissolved in 1 l of distilled water to obtain the lime solution [4]. Then, the testing samples were prepared by mixing 1 g of pozzolan with 75 ml of the previously obtained lime solution. Prepared testing samples were left in a sealed plastic bottle in an oven at 40 °C for 1, 3, 7 and 28 days. After a set time, samples

Table 2
Compositions of studied samples for SAI and ASR tests.

Composition	Solid compounds, mass part							Plasticiser	W/(C + P)
	CEM	Pozzolans					Quartz sand		
		SF	EG	KG	MK	FA			
C-REF	1.00						3.00	0.0	0.50
C-SF	0.80	0.20						1.8	0.50
C-EG	0.80		0.20					0.9	0.50
C-KG	0.80			0.20				0.2	0.50
C-MK	0.80				0.20			0.2	0.50
C-FA	0.80					0.20		0.0	0.50

were filtered and titrated to quantify the amount of fixed lime. Results are reported as mmol CaO fixed or % total CaO fixed per 1 g of tested pozzolan.

The procedure of SAI testing was based on BS 3892 [19]. Control mortar cubes were prepared by mixing 1350 g quartz sand, 450 g CEM and 225 ml water by hand mixer for 5 minutes. Test samples were prepared in the same manner, except that 20% of the CEM was replaced with the pozzolan. All compositions are presented in Table 2. Flow tests were carried out on pastes, according to EN 1015-3 [23]. The water to binder ratio was altered to give the mixture the same flow properties as the control mortar (±5 mm). Mortar pastes were then remixed for 30 s and cast into six50 mm cubes with the aid of a vibrating table. Samples were de-moulded after 24 h and placed in a water bath at 20 ± 2 °C for 6 or 27 days. They were then removed from the bath, surface dried and tested for 7- or 28-day compressive strength. Strength results reported are the averages of three tests and are presented as percentage strength relative to the control mortar with the SAI reported as:

$$SAI = {}^{A}/_{B} \cdot 100\% \quad (1)$$

where A is the unconfined compressive strength of the test pozzolan specimen (MPa), and B is the unconfined compressive strength of the control mortar (MPa). According to BS 3892, SAI results greater than 0.80 after 28 days are indicative of positive pozzolanic activity for FA for a cement replacement of 30%. However, ASTM C618 requires an SAI greater than 0.75 after 7 and 28 days for FA and natural pozzolans at the cement replacement of 20% [24].

The alkali–silica reaction (ASR) test was performed according to RILEM TC 106-2 – detection of potential alkali-reactivity of aggregates – the ultra-accelerated mortar-bar test [25] for six cement mortar compositions (Table 2). The 24 hour-old (±2

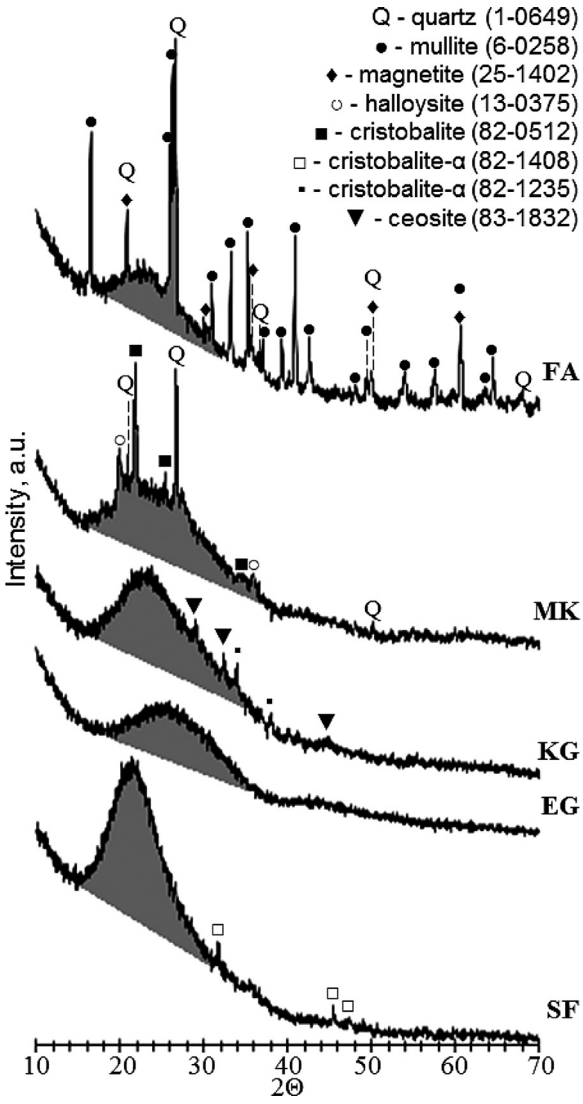

Fig. 1. XRD patterns of studied pozzolans.

h) specimens were hardened in water at 80 °C for 24 h, and the initial sample length was measured right after that. Finally, samples were kept in 1 M NaOH solution at 80 °C, and ASR expansions were measured for 14 days. Six specimens were measured for each mixture and mean value calculated.

3. Results and discussions

3.1. Determination of the pozzolanic activity by direct test methods

All chosen industrial by-products (EG, KG, MK), as well as SF and FA, had silica and aluminium oxide in their chemical composition (Table 1), with SiO_2 from 48.0 to 98.4% and Al_2O_3 from 0.2% to 39.6%. The SF presented the highest SiO_2 amount – 98.4%, while the industrial by-product with the highest silica dioxide amount was KG with 76.1%. MK had the lowest SiO_2 amount at 48.0% while EG had 52.3% and FA had 50.8% SiO_2. Al_2O_3 contributes to higher pozzolanic reactivity at an initial stage, since the formed aluminates react faster than silicates, but the final strength is lower [26] [17]. In such a way, MK displayed the most Al_2O_3 in its composition with 39.6%, followed by FA with 27.5% and EG with 14.1%. However, a certain fraction may not be active. Therefore, the chemical composition cannot be investigated alone; it needs to take the mineralogy and amorphousness of the pozzolan into consideration [17].

X-ray diffractograms of studied industrial by-products and the commercial pozzolan are presented in Fig. 1. As expected, all studied materials had amorphous or vitreous phases that were indicated by halo ranging from 15 to 35 degrees. As the crystalline silica and aluminium silicates are chemically inert (quartz [27], mullite [28], halloysite [29], cristobalite [30] and coesite [31]), only amorphous (as well as vitreous in case of FA) silicates and aluminium silicates can have glassy reactive silica and alumina [32]. The amorphous phase of SF presented, showing minor crystalline phase peaks of cristobalite-α (SiO_2). Meanwhile, EG only presented an amorphous phase by halo at 20–35 degrees, but KG presented an amorphous phase by halo at 15–35 degrees with some crystalline phases of cristobalite-α (SiO_2) and coesite (SiO_2). The peak of the amorphous phase of EG presented at a higher 2Θ degree than KG and SF because of the higher amount of amorphous Al_2O_3 in its composition. The amorphous phase of MK presented by halo at 15–30 degrees and crystalline phases of quartz (SiO_2), halloysite ($Al_2Si_2O_5(OH)_4$) and cristobalite (SiO_2) were detected. The FA presented a vitreous phase by halo at 15–30 degrees, with crystalline phases of quartz (SiO_2), mullite ($3Al_2O_3 \cdot 2SiO_2$) and magnetite (Fe_2O_3).

According to results of micro-granulometry (Fig. 2), 99% of the particles in the commercial pozzolan SF were smaller than 45 μm, while the studied FA had 66%, but the other three studied industrial by-products had similar results to SF, with KG having 98% but EG and MK having > 92%. According to standards (EN 450 for FA), more than 60 wt.% of particles should be < 45 μm to satisfy fineness requirements [33]. Also, according to ASTM C618, fine ground glasses under 45 μm qualify as pozzolan due to their fine particle nature [34].

Results on the BET specific surface area of the studied materials are presented in Fig. 3. The highest specific surface area presented is SF, with 21.5 m^2/g, while MK shows 5.5 m^2/g, but both glasses EG and KG show 0.7 m^2/g, and FA shows 0.5 m^2/g. From the point of specific surface area, MK is the most promising pozzolanic additive of the studied industrial by-products. It is generally accepted that an increase of specific area or decrease in particle size exposes a greater surface to chemical reactions, enhancing reactivity. The increased fineness could bring some adverse side effects as well; Walker and Pavia conclude that the specific surface area of a pozzolan governs the water demand of the paste [17]. To avoid the negative effects of using extra water to satisfy workability requirements, highly effective superplasticisers are often used with pozzolans [35].

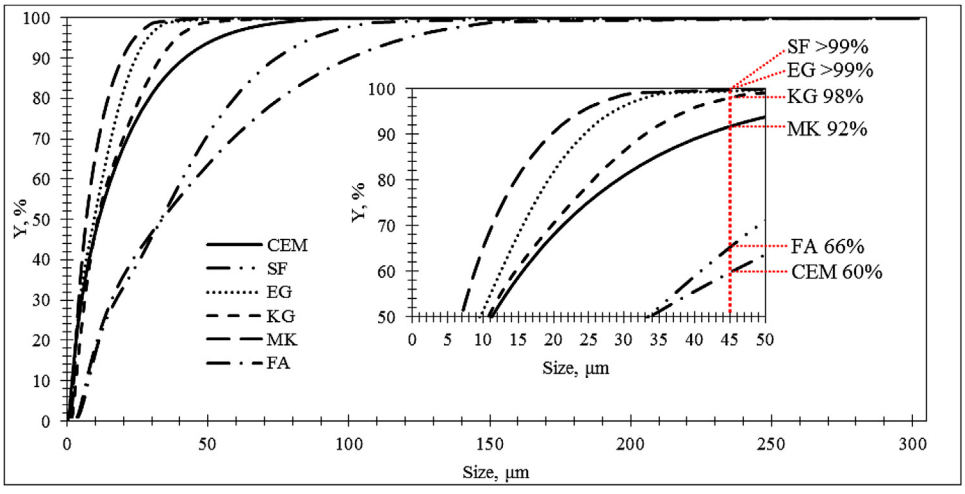

Fig. 2. Particle size distribution of studied industrial by-products, silica fume and Portland cement.

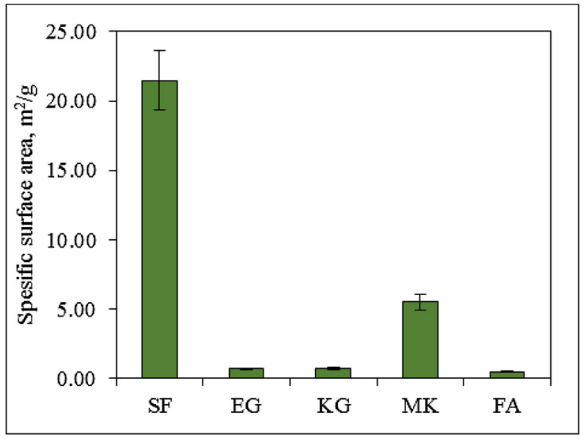

Fig. 3. Specific surface area of studied pozzolans, m^2/g.

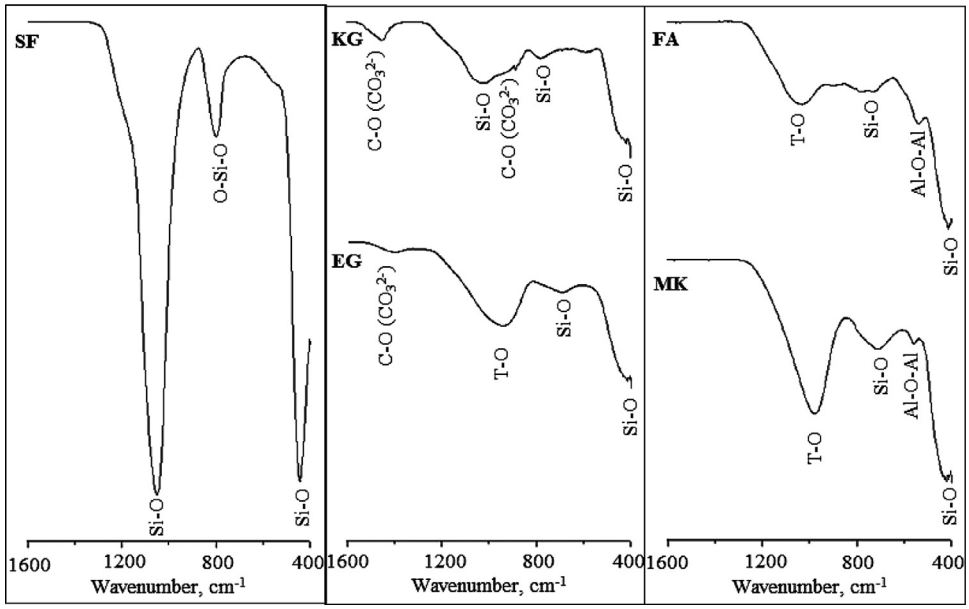

Fig. 4. FTIR analyses for studied industrial by-products and commercial pozzolan.

The infrared spectra (FTIR) of the original raw pozzolans are presented in Fig. 4. The overall spectrum of crystalline material has much sharper bands than the spectrum of amorphous material. Therefore, FTIR could characterise the amorphous phase presence when quantitative results cannot be obtained. The FTIR spectrum of SF consists of three intensive main bands. The band at 1048 cm^{-1} and the band at 443 cm^{-1} present the amorphous phase of cristobalite (Si–O stretching and Si–O bending), but the band at 779 cm^{-1} presents the crystalline phase of cristobalite-α (Si–O bending) [36] [37].

It was difficult to determine the functional groups present on EG and KG; hence, weak transmittance peaks were observed [38]. The C–O bond asymmetric stretching vibration band was detected in the FTIR spectrum of KG and EG, appearing at 1440 cm^{-1} and 1394 cm^{-1}, respectively [39].

In the case of MK, the main band was located at 974 cm^{-1}, which corresponded to the internal vibrations in the TO_4 tetrahedral (T = Al, Si). The two bands at 709 cm^{-1} and 427 cm^{-1} corresponded with the presence of quartz [40], but the band at 557 cm^{-1}, corresponding to the Si–O–Al banding vibrations, presented the halloysite [41].

The FTIR spectrum for FA contained the main wide and intense band characteristics of the internal vibrations in the TO_4 tetrahedral (T = Al, Si), which peaks around 1031 cm^{-1} and is associated with T–O bond asymmetric stretching vibrations. The presence of quartz in FA gave rise in the FTIR spectrum to bands located at 773–734 cm^{-1} (double band) and 419 cm^{-1}. The presence of mullite, in turn, was responsible for a band around 544 cm^{-1} (octahedral aluminium present in mullite) [42].

Fig. 5 indicates that all studied materials present pozzolanic activity, as all tested materials lie below the solubility curve of $Ca(OH)_2$. To describe the Frattini test results more comparably with other test methods, it is useful to quantify the results

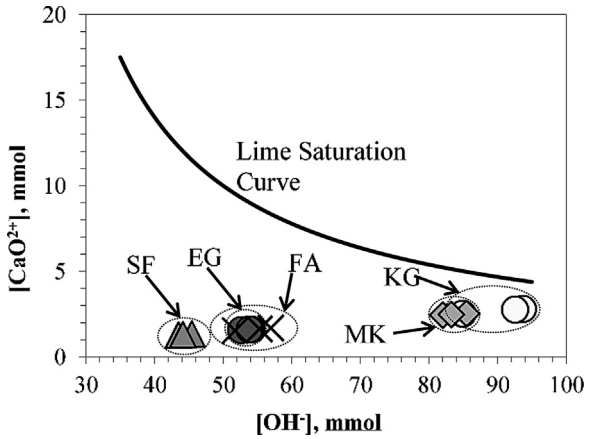

Fig. 5. The pozzolans reactivity studied for industrial by-products and commercial pozzolan by Frattini test method.

obtained by the Frattini test. This was achieved by considering the distance of the data points from the lime solubility curve and the zero point on the vertical axis at the given OH^-. The theoretical maximum of the CaO concentration, which can be found by the calculation given in the EN 196-5, was curved to plot the lime solubility. The calcium concentrations in the tested samples were compared with the theoretical maximum CaO, so the percentages of CaO removed were obtained.

The obtained quantification results show that, according to the Frattini test, the commercially-available pozzolanic additive SF removed 89.0% of [CaO], while the studied industrial by-products presented lower bonding of [CaO], with EG at 82.1%, KG at 43.3%, MK at 50.8% and FA at 81.4%.

The saturated lime test results are summarised in Fig. 6. Accounting for the control baseline, it is clear that all studied industrial by-products, as well as silica fume, showed pozzolanic activity in the saturated lime test. There was a difference in the rate of lime fixation between the studied materials for 28 days. SF removed lime the fastest, removing 78% on the first testing day. The studied industrial by-products removed 23–46% of lime on the first testing day (EG: 23%, KG: 46%, MK: 41% and FA: 23%). However, after 28 days, there were no noteworthy differences between SF (94%), MK (97%) and KG (94%).

The particle size distribution (Fig. 2) might have caused a slower reaction between FA and lime. Only 66% of the FA particles were smaller than 45 μm, and it takes more time for bigger particles to take part in a reaction. In the case of EG, the lower reaction rate could have been caused by its chemical composition (Table 1). Also, the relatively high CaO amount (23.4%) might have prevented an objective assessment of the true reaction rate between EG and lime.

3.2. Description of the pozzolanic reactivity by an indirect test method

The physical and mechanical properties of the studied cement mortar are summarised in Table 3. The reference mortar's compressive strength was 31.2 MPa on day 7 and 40.0 MPa on day 28. Fig. 7 shows that all tested specimens containing industrial by-products (EG, KG, MK and FA) caused a decrease in compressive strength on day 7, relative to the reference, while commercially-available pozzolan SF caused an increase in the compressive strength on day 7. On day 28, mortars of

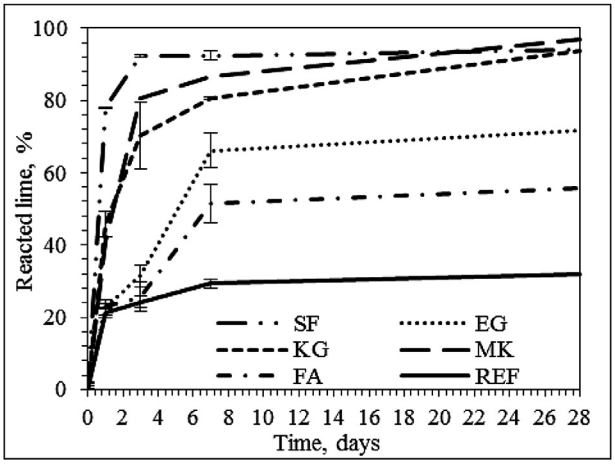

Fig. 6. The pozzolanic reactivity of studied materials by the saturated lime test.

Table 3
The results of the physical and mechanical properties of studied cement mortars.

Composition	Material Density, kg/m^3	Water Absorption by mass,%	Compressive Strength f_c, MPa	
			on Day 7	on Day 28
C-REF	1970 ± 18	9.0 ± 0.2	31.2 ± 1.2	40.0 ± 1.7
C-SF	1900 ± 15	9.7 ± 0.2	34.9 ± 1.0	51.5 ± 2.2
C-EG	1930 ± 6	9.2 ± 0.1	27.7 ± 0.7	40.3 ± 1.5
C-KG	1860 ± 15	9.8 ± 0.1	16.9 ± 0.9	21.3 ± 2.5
C-MK	1920 ± 8	9.1 ± 0.1	30.1 ± 1.1	41.6 ± 0.6
C-FA	1940 ± 11	9.1 ± 0.1	23.3 ± 1.4	32.0 ± 1.1

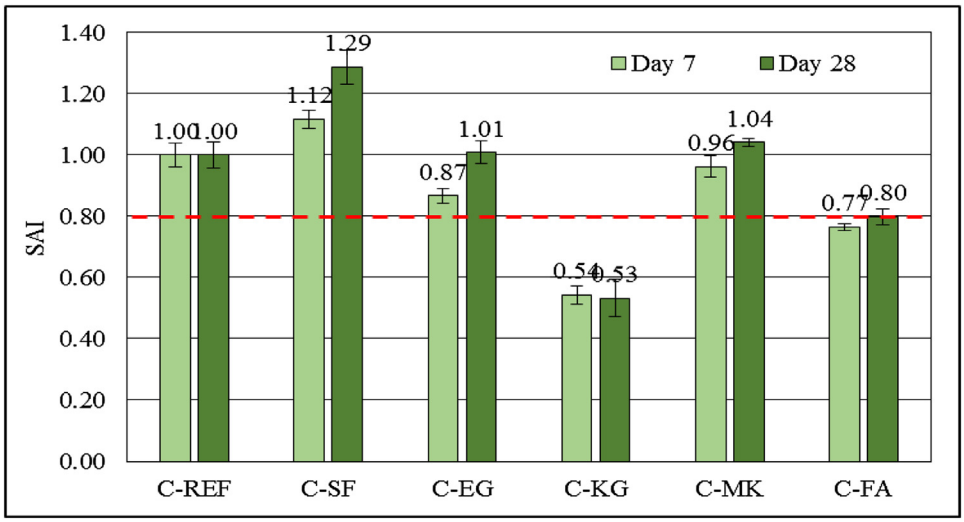

Fig. 7. The SAI results of the studied industrial by-products and commercial pozzolan.

C-EG and C-MK provided higher compressive strength compared to the reference mortar. The relatively low SAI of the C-KG can be explained by the high content of alkalis in KG; 21.0% of KG was sodium dioxide (Table 1).

The ASR is one of the major causes of premature concrete deterioration. The structural damages of concrete due to the ASR can be mitigated by substituting finely reactive materials such as pozzolanic additives with Portland cement [43]. Traditionally, Portland cement is the main source of alkalis in concrete, while the alkali content (Na_2O_{eq}) is limited by cement production standards. It is reported that pozzolanic additives can limit the ASR as they reduce the alkali and OH- concentration in the pore solution [44] [45]. However, there might also be some pozzolans that increase the alkalinity of the solution and may not be able to reduce the expansion of reactive aggregate concretes. In this study, the equivalent Na_2O content in the Portland cement was 0.9%, but in the studied industrial by-products and commercially-available pozzolanic additive, it was as follows: SF: 0.3%, EG: 0.9%, KG: 21.0%, MK: 8.9% and FA: 2.0%. This should be taken into account in concrete mixture design, as it has been reported that no deleterious ASR was generated when the water-soluble alkali content of the Portland cement (Na_2O_{eq}) was less than 1.5 kg/m^3 or 0.55% by mass [46]. The ASR results in a silicate gel, which is hygroscopic and absorbs moisture from the internal concrete structure, which causes the expansion of the silica gel. The testing standard RILEM TC 106-2 recommends an expansion limit of 0.054%, while Broekmans mentions that an expansion of 0.04% to 0.05% is deleterious [47].

The ASR results are given in Fig. 8. The final relative expansion of all studied mortars, except C-KG, ranged from 0.004 to 0.054%, which satisfies the limits given in the description of the testing method. The mortar sample C-KG proved to be highly expansive in an alkali environment, and the relative deformation exceeded the limit recommended by RILEM TC 106-2 on the first testing day, which is analogous to the case of the compressive strength because of the high alkali content in KG (Table 1).

For prismatic samples placed in a testing solution (1 M NaOH) or water at 80 °C, the compressive strength difference (ΔRC) after 14 d varied from −6.5% to +2.2% (Fig. 8). Strength changes due to excess alkalis in the curing medium were not detected. Compressive strength changes alone cannot be used as an evaluation indicator of pozzolanic additives as the silicate gel (ASR product) can fill the cracks and provide smooth stress distribution across the material cross-section. The water absorption was relatively similar for all studied mortars (9.0–9.8%, shown in Table 3). The lowest expansion, presented by C-SF, can be explained by the low equivalent Na_2O content of 0.3%. The CEM and EG had the same amount of Na_2O_{eq} – 0.9%, which explains the similar results of ASR - expansion of C-CEM (0.054%) and C-EG (0.050%) on the fourteenth testing day.

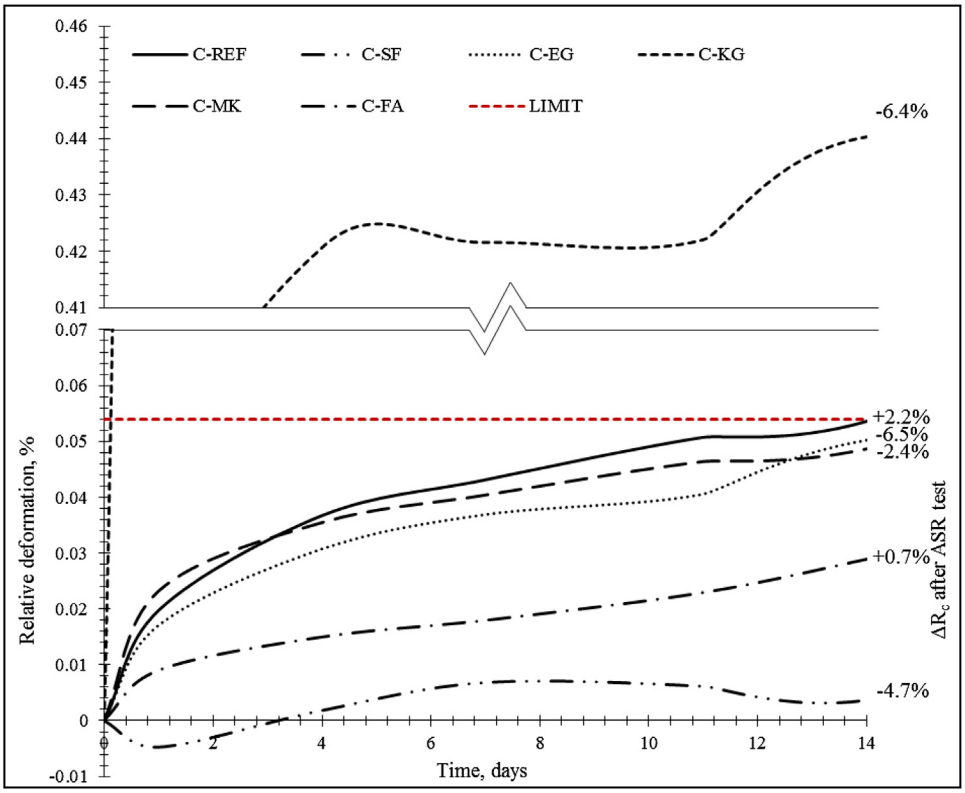

Fig. 8. The ASR results of the studied industrial by-products and commercial pozzolan.

3.3. The comparison of test methods

By analysing the selected materials with a single yet well-known test method as described before, many factors could lead to false assessment. Only a complex analysis of the selected raw materials and testing methods provides a trusted overall evaluation of potential pozzolanic material efficiency. To save time and resources, it is useful to start with simple and fast evaluation methods, avoiding long tests. Even if initial tests show promising results, they do not guarantee improved results in mortar or concrete, because alkalis have little no or impact on pozzolanic reactions while they have a significant impact on ASRs, which impacts mechanical properties as well.

The Frattini test and saturated lime test results proved to be mutually different (Fig. 9). In the case of SF, the results of both pozzolanic activity testing methods have a 5% difference. By Frattini test, SF removed 89% of CaO, while by saturated lime

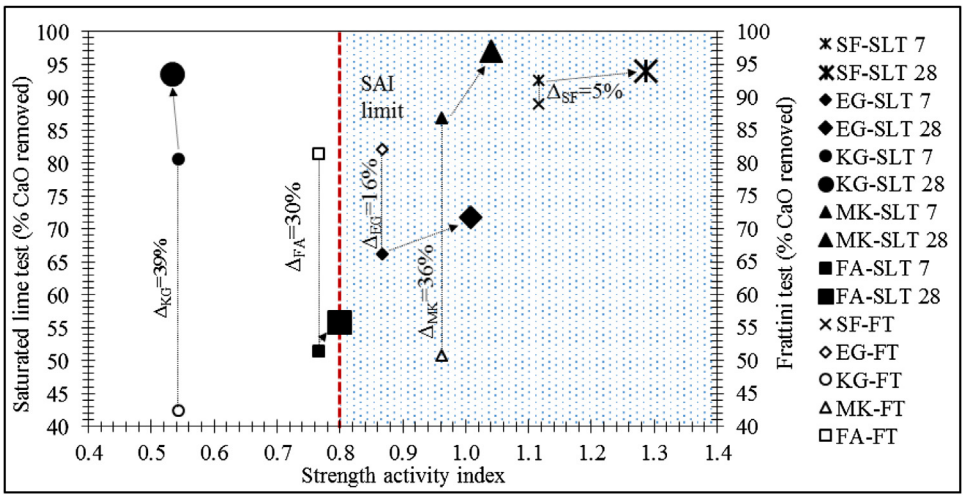

Fig. 9. The relation between Frattini test (FT), saturated lime test (SLT) and SAI on Day 7 and Day 28.

test, it removed 93%, which could be an acceptable difference. Other studied pozzolanic additives showed significant differences between the results of the Frattini test and the saturated lime test.

All other tested pozzolanic materials with $SiO_2 \leq 76.1\%$ presented a considerable divergence of removed CaO amounts when tested by the Frattini test and the saturated lime test. First, two noteworthy differences between both testing methods should be taken into account: the results of Frattini test were obtained after eight days of the reaction process, but the saturated lime test results were taken after seven days, which might explain the divergence of results within the margin of error (i). For the saturated lime test, 0.15 g of pure $Ca(OH)_2$ per 1 g of tested material was used, but in the Frattini test, for 1 g of tested material, 4 g of Portland cement was used to show the amount of CaO that could be removed by pozzolanic material (ii). According to the Frattini test, the pozzolanic material and $Ca(OH)_2$ ratio is 1:0.15, while for the saturated lime test, it is about 1:1, as it is known that 25% of the original cement mass is present as $Ca(OH)_2$ after complete hydration [4]. Comparison of the Frattini and saturated lime tests (Fig. 9) shows that the same mechanism reaction caused by pozzolanic additives did not occur in saturated $Ca(OH)_2$ and CEM-I solutions. The presence of free alkali ions (Na^+ and K^+) turned down the solubility of $Ca(OH)_2$. Also, the pH of the $Ca(OH)_2$ solution is lower than the pH of the CEM-I solutions (12.4 and 13.0, respectively).

3.4. A roadmap for pozzolanic material evaluation for concrete application

The summary of the procedures offered to evaluate industrial by-product evaluation for concrete application is given in Fig. 10. First of all, the general facts about the by-product should be collected. The origin, amount available, delivery

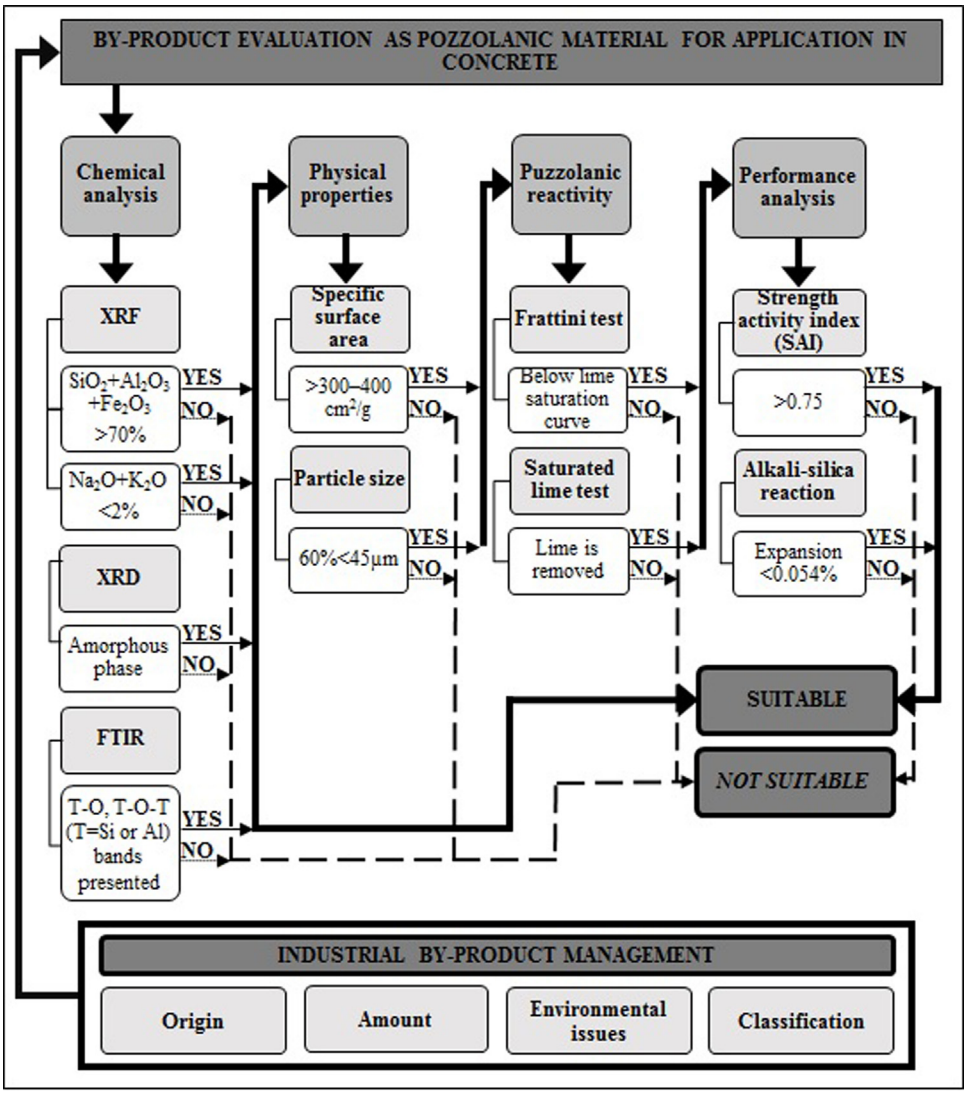

Fig. 10. Roadmap for by-product evaluation for application in concrete.

conditions, hazardous impurities, etc. should be determined [34]. If by-products pass these criteria, the investigation of the by-product as a possible pozzolanic material should be evaluated. The most basic test methods to start by-product analysation are associated with the material's physical and chemical analyses. The chemical composition detected by XRF indicates the amounts of SiO_2, Al_2O_3 and Fe_2O_3, which are typically characteristic for pozzolanic materials. The mentioned compounds should be > 70%, as according to standard requirements given for FA in EN 450 (for class F fly ash) [33]. As tested in this research, the glass by-product's chemical composition could fall below the mentioned border, and in the literature, it was 66.8% for EG in this research or could be as low as 60.5% for glass powder [48]. Another important factor is the content of impurities, such as organics, alkalis and sulphates, which should be limited [49]. Mineral compounds can also be in crystalline form, which can be indicated by the XRD. Traditionally, crystalline compounds do not participate in pozzolanic reactions. An alternative method of determining the fraction of the reactive phase of the starting materials is using selective chemical attack and titration, based on EN 196-2, but this method is time-consuming [50]. If the chemical composition falls between the requirements, the physical properties of the powder must be characterised, as fine-grained powder materials with fineness > 300 cm^2/g and more than 60 wt.% of particles < 45 μm are needed (described in EN 450 for FA) [33]. The FA investigated in this research had a specific surface area of 500 cm^2/g, which was the coarsest material investigated. All materials investigated fell within these parameters. If the material is coarser, additional ball or collision milling should be performed. Further testing is associated with direct test methods to describe the pozzolanic reactivity, which characterises the possibility of attracting lime from a saturated lime solution or lime coming from cement hydration products. If a material attracts free lime, there is a possibility of pozzolanic reactions occurring in the concrete structure. All materials investigated in this research proved to be reactive with lime. Further testing is associated with performance analysis. Performance analysis provides quantitative results of strength gain during hardening. 20 wt.% replacement of cement by pozzolan should give > 75% strength than that of reference at 28 d and > 85% at 90 d, according to EN 450 [33]. If the alkali or silica content is high, possible deleterious ASRs may occur, which should be taken into account when selecting by-products as possible pozzolanic materials for concrete [51].

The results from this research were evaluated according to the proposed roadmap (Table 4). It can be seen that only SF completely satisfies the requirements given in the roadmap proving itself as the most advanced supplementary cementitious material for use in concrete production. This is also formulated in the design methods for concrete (EN 206), where k-value for silica fume of class 1 conforming to EN 13263-1 is in range from 1-2 [52,53]. The FA evaluated in this research has a higher alkali content than allowed in ASTM C 618 and AASHTO M 295. The limit is 1.5% while the common range of alkalis in FA could be from 0.75% to 2.75% [54]. Also, EG failed to reach the border values given by the XRF test (SiO_2, Al_2O_3, Fe_2O_3 < 70% as for F-class FA), the rest of the tests showed satisfactory results and positive performance of EG is an important finding of this research. In this case, EG could be compared to C-class FA. In the case of C-class FAs, which generally contain significant percentages of calcium compounds, the sum of SiO_2, Al_2O_3 and Fe_2O_3 is only required to be greater than 50% [55]. The total content of SiO_2, Al_2O_3, Fe_2O_3 and CaO in EG is 90.2%. The KG and MK were characterised by a high Na_2O content, which could be the most reliable reason it did not pass the SAI and ASR tests. In the case of MK, the increase of total alkalis in concrete could be reached even with a low MK dosage; therefore, the application of MK could be limited. By following test methods suggested in roadmap, different pozzolanic materials showed good compliance with current state-of the art and standards applied for evaluation of supplementary cementitious materials for use in concrete production. The by-products or waste products from industrial processes proved to be suitable for use as cementitious materials while strict quality control should be maintained to guarantee the quality of the materials.

Table 4
Compliance of tested by-products and commercial materials to the roadmap proposed in Fig.10.

Roadmap criteria	Material evaluated				
	SF	FA	MK	EG	KG
XRD amorphous phase	Yes	Yes	Yes	Yes	Yes
XRF, SiO_2, Al_2O_3, Fe_2O_3 > 70%	Yes (98.6)	Yes 84.7)	Yes (88.5)	**No (66.8)**	Yes (79.0)
Alkali content Na_2O_{ek} < 1.5%	Yes 0.3	**No 2.0**	**No 8.9**	Yes 0.9	**No 21.0**
FTIR (Si, Al, Fe bonds)	Yes	Yes	Yes	Yes	Yes
Particle size < 0.45 μm more than 60%	Yes (99%)	Yes (66%)	Yes (92%)	Yes (99%)	Yes (98%)
Fineness > 300–400 cm^2/g	Yes (21500)	Yes (500)	Yes (5500)	Yes (700)	Yes (700)
Frattini test	Pass	Pass	Pass	Pass	Pass
Lime test	Pass	Pass	Pass	Pass	Pass
SAI > 75%	Yes (129)	Yes (80)	Yes (104)	Yes (101)	**No (53)**
ASR < 0.054	Yes (0.004)	Yes (0.029)	Yes (0.049)	Yes (0.050)	**No (0.440)**

4. Conclusion

This study aimed to establish a fast, reliable, cost-effective technology roadmap for the concrete industry to introduce new pozzolanic materials originating mostly from industrial by-products to concrete production. The multi-objective optimisation testing programme was employed to design the pozzolanic material evaluation roadmap including nine test-passing objectives. Experimental data on five different possible pozzolans was acquired and evaluated through the suggested roadmap. Analyses showed the conflict in the effects of different aspects of some recommended testing methods, including chemical and physical characterisation of possible pozzolans as well as noncompliance in reactivity and performance tests. The appearance of pozzolans such as fineness can be adjusted by proper pre-treatment such as milling therefor this criterion could be easily adjusted. All selected pozzolans proved to be reactive according to direct testing methods of pozzolans (Frattini test and saturated lime test). Most of the tested pozzolanic materials failed at least one of nine test criteria, and only silica fume passed all the criteria. The most critical aspect of pozzolanic materials tested were alkali content and their performance in cement composites, such as strength activity index and expansion due to alkali-silica reactions. The results confirm that only a complex testing solution brings a reliable evaluation of industrial by-products, and the elaborated roadmap maximises the possible benefits of finding new pozzolans for safe and effective use in concrete. The surprising finding was associated with the positive performance of alkali-free E-glass (EG), which proved to be effective pozzolan with the performance comparable to the one of silica fume, while high alkali content silica glass showed opposite effect on concrete performance resulting with high expansion deformations and cracking of the samples.

Declaration of Competing Interest

None.

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References

[1] EUROPEAN COMMISSION, European Commission: Roadmap to a Resource Efficient Europe, (2011) 21.
[2] ASTM Committee C09.91, ASTM C125-19 Standard Terminology Relating to Concrete and Concrete Aggregates, Annu. B. ASTM Stand, vol. 04.02(2019), doi:http://dx.doi.org/10.1520/C0125-15A.
[3] J. Setina, A. Gabrene, I. Juhnevica, Effect of pozzolanic additives on structure and chemical durability of concrete, Procedia Eng., (2013), doi:http://dx.doi.org/10.1016/j.proeng.2013.04.127.
[4] S. Donatello, M. Tyrer, C.R.R. Cheeseman, Comparison of test methods to assess pozzolanic activity, Cem. Concr. Compos. 32 (2010) 121–127, doi:http://dx.doi.org/10.1016/j.cemconcomp.2009.10.008.
[5] G. Quercia, P. Spiesz, G. Hüsken, J. Brouwers, Effects of Amorphous Nano-Silica Additions on Mechanical and Durability Performance of Scc Mixtures, Proc. Int. Congr. Durab. Concr. (ICDC 2012 (2012) 15.
[6] D. Bajare, G. Bumanis, L. Upeniece, Coal combustion bottom ash as microfiller with pozzolanic properties for traditional concrete, Procedia Eng., (2013), doi:http://dx.doi.org/10.1016/j.proeng.2013.04.022.
[7] H. El-Diadamony, A.A. Amer, T.M. Sokkary, S. El-Hoseny, Hydration and characteristics of metakaolin pozzolanic cement pastes, HBRC J. (2018), doi:http://dx.doi.org/10.1016/j.hbrcj.2015.05.005.
[8] M. Elbar, Y. Senhadji, A.S. Benosman, H. Khelafi, M. Mouli, Effect of thermo-activation on mechanical strengths and chlorides permeability in pozzolanic materials, Case Stud. Constr. Mater. (2018), doi:http://dx.doi.org/10.1016/j.cscm.2018.04.001.
[9] Y.T. Tran, J. Lee, P. Kumar, K.H. Kim, S.S. Lee, Natural zeolite and its application in concrete composite production, Compos. Part B Eng. (2019), doi:http://dx.doi.org/10.1016/j.compositesb.2018.12.084.
[10] X.Y. Wang, K.B. Park, Analysis of compressive strength development of concrete containing high volume fly ash, Constr. Build. Mater. (2015), doi:http://dx.doi.org/10.1016/j.conbuildmat.2015.08.099.
[11] İ. Ustabaş, A. Kaya, Comparing the pozzolanic activity properties of obsidian to those of fly ash and blast furnace slag, Constr. Build. Mater. (2018), doi:http://dx.doi.org/10.1016/j.conbuildmat.2017.12.185.
[12] M. Bediako, Pozzolanic potentials and hydration behavior of ground waste clay brick obtained from clamp-firing technology, Case Stud, Constr. Mater. (2018), doi:http://dx.doi.org/10.1016/j.cscm.2017.11.003.
[13] E.T. Bueno, J.M. Paris, K.A. Clavier, C. Spreadbury, C.C. Ferraro, T.G. Townsend, A review of ground waste glass as a supplementary cementitious material: A focus on alkali-silica reaction, J. Clean. Prod. 257 (2020) 120180, doi:http://dx.doi.org/10.1016/j.jclepro.2020.120180.
[14] G. Pachideh, M. Gholhaki, H. Ketabdari, Effect of pozzolanic wastes on mechanical properties, durability and microstructure of the cementitious mortars, J. Build. Eng. 29 (2020), doi:http://dx.doi.org/10.1016/j.jobe.2020.101178.
[15] S.K. Agarwal, Pozzolanic activity of various siliceous materials, Cem. Concr. Res. 36 (2006) 1735–1739, doi:http://dx.doi.org/10.1016/j.cemconres.2004.06.025.
[16] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Assessment of pozzolanic activity of different calcined clays, Cem. Concr. Compos. 37 (2013) 319–327, doi:http://dx.doi.org/10.1016/j.cemconcomp.2013.01.002.
[17] R. Walker, S. Pavía, Physical properties and reactivity of pozzolans, and their influence on the properties of lime-pozzolan pastes, Mater. Struct. Constr. 44 (2011) 1139–1150, doi:http://dx.doi.org/10.1617/s11527-010-9689-2.
[18] G. Shakhmenko, D. Bajare, I. Juhnevica, N. Toropovs, J. Justs, A. Gabrene, Properties and Composition of Concrete Containing Diverse Pozzolanic Admixtures, 4th Int. Conf. Civ. Eng. Proc. Part I, (2013) .
[19]] British Standards Institution, BS EN 3892 Part 1. Specification for pulverized-fuel ash for use with Portland cement, (1997) .
[20] J. Brame, C. Griggs, Surface Area Analysis Using the Brunauer-Emmett-Teller (BET) Method Scient, Eng. Res. Dev. Cent. (2016) doi:39180-6199.
[21] British Standards Institution, BS EN 196-5:2011 Methods of testing cement. Pozzolanicity test for pozzolanic cement, (2011) .
[22] A. Scrivener, Favier Karen, Calcined Clays for Sustainable Concrete: Proceedings of the 1st International Conference on Calcined Clays for Sustainable Concrete, (2015) .

[23] BS EN 1015-3, Methods of test for mortar for masonry. Determination of Consistence of Fresh Mortar (by flow table), London, (1999) .
[24] ASTM, C 618-12a Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, ASTM Int., (2012), doi:http://dx.doi.org/10.1520/C0618-12A.
[25] B-TC 106-3-Detection of potential alkali-reactivity of aggregates-Method for aggregate combinations using concrete prisms, Mater. Struct. (2000), doi:http://dx.doi.org/10.1007/bf02479698.
[26] H. Paiva, A. Velosa, P. Cachim, V.M. Ferreira, Effect of pozzolans with different physical and chemical characteristics on concrete properties, Mater. Constr. 66 (2016) e083, doi:http://dx.doi.org/10.3989/mc.2016.01815.
[27] G. Bumanis, D. Bajare, Compressive Strength of Cement Mortar Affected by Sand Microfiller Obtained with Collision Milling in Disintegrator, Procedia Eng. (2017), doi:http://dx.doi.org/10.1016/j.proeng.2017.02.037.
[28] J.K. Bibby, N.L. Bubb, D.J. Wood, P.M. Mummery, Fluorapatite-mullite glass sputter coated Ti6Al4V for biomedical applications, J. Mater. Sci. Mater. Med, Springer, 2005, pp. 379–385, doi:http://dx.doi.org/10.1007/s10856-005-6975-6.
[29] F. Hart, Advances in Medical Uses for Alumino Silicate Clay Minerals, Focusing on Naturally Occurring Kaolin, Smectites and Halloysite, (2014) 2, (n.d.) https://www.linkedin.com/pulse/20140711184747-121149092-advances-in-medical-uses-of-kaolin-and-smectites/(accessed April 23, 2020).
[30] Pozzolanic Activity - an overview | ScienceDirect Topics, (n.d.). https://www.sciencedirect.com/topics/engineering/pozzolanic-activity (accessed April 23, 2020).
[31] Crystalline Silica: The Science | Safe Silica, (n.d.). https://safesilica.eu/crystalline-silica-the-science/ (accessed April 23, 2020).
[32] M. Davraz, L. Gunduz, Engineering properties of amorphous silica as a new natural pozzolan for use in concrete, Cem. Concr. Res. 35 (2005) 1251–1261, doi:http://dx.doi.org/10.1016/j.cemconres.2004.11.016.
[33] BS EN 450-451:2012 - Fly ash for concrete. Definition, specifications and conformity criteria, (n.d.). https://shop.bsigroup.com/ProductDetail?pid=000000000030216589 (accessed July 31, 2020).
[34] A. Seco, F. Ramirez, L. Miqueleiz, P. Urmeneta, B. Garca, E. Prieto, V. Oroz, Types of Waste for the Production of Pozzolanic Materials – A Review, Ind. Waste, (2012), doi:http://dx.doi.org/10.5772/36285.
[35] G. Bumanis, D. Bajare, A. Korjakins, Durability of High Strength Self Compacting Concrete with Metakaolin Containing Waste, Key Eng. Mater. 674 (2016) 65–70, doi:http://dx.doi.org/10.4028/www.scientific.net/KEM.674.65.
[36] V. Correcher, J. Garcia-Guinea, M.A. Bustillo, R. Garcia, Study of the thermoluminescence emission of a natural α-cristobalite, Radiat. Eff. Defects Solids. (2009), doi:http://dx.doi.org/10.1080/10420150802270995.
[37] A. Bosio, A. Gianoncelli, A. Zacco, L. Borgese, N. Rodella, D. Zanotti, L.E. Depero, G. Siviero, A. Cinosi, P.A. Bingham, E. Bontempi, A new nanotechnology of fly ash inertization based on the use of silica gel extracted from rice husk ash and microwave treatment, Proc. Inst. Mech. Eng. Part N J. Nanoeng. Nanosyst. 228 (2014) 27–32, doi:http://dx.doi.org/10.1177/1740349913490683.
[38] V.R. Arun prakash, A. Rajadurai, Inter laminar shear strength behavior of acid, base and silane treated E-glass fibre epoxy resin composites on drilling process, Def. Technol. 13 (2017) 40–46, doi:http://dx.doi.org/10.1016/j.dt.2016.11.004.
[39] I. Garcia-Lodeiro, A. Palomo, A. Fernández-Jiménez, D.E. Macphee, Compatibility studies between N-A-S-H and C-A-S-H gels. Study in the ternary diagram Na2O–CaO–Al2O3–SiO2–H2O, Cem. Concr. Res. 41 (2011) 923–931, doi:http://dx.doi.org/10.1016/j.cemconres.2011.05.006.
[40] G. Bumanis, L. Vitola, D. Bajare, L. Dembovska, I. Pundiene, Impact of reactive SiO2/Al2O3 ratio in precursor on durability of porous alkali activated materials, Ceram. Int. 43 (2017) 5471–5477, doi:http://dx.doi.org/10.1016/j.ceramint.2017.01.060.
[41] Z. Yunsheng, S. Wei, C. Qianli, C. Lin, Synthesis and heavy metal immobilization behaviors of slag based geopolymer, J. Hazard. Mater. 143 (2007) 206–213, doi:http://dx.doi.org/10.1016/j.jhazmat.2006.09.033.
[42] M. Criado, A. Fernández-Jiménez, A. Palomo, Alkali activation of fly ash: Effect of the SiO2/Na2O ratio. Part I: FTIR study, Microporous Mesoporous Mater. 106 (2007) 180–191, doi:http://dx.doi.org/10.1016/j.micromeso.2007.02.055.
[43] K.-Y. Show, J.-H. Tay, D.-J. Lee, Cement Replacement Materials, Sustain. Sludge Manag, (2018), doi:http://dx.doi.org/10.1142/9789813238268_0005.
[44] K.E. Kurtis, P.J.M. Monteiro, S.M. Madanat, Empirical models to predict concrete expansion caused by sulfate attack, ACI Struct. J. (2000), doi:http://dx.doi.org/10.14359/818.
[45] N. Attoh-Okine, F. Atique, Service Life Assessment of Concrete with ASR and Possible Mitigation, (2006) .
[46] M.L. Leming, B.Q. Nguyen, Limits on alkali content in cement - Results from a field study, Cem. Concr. Aggregates. 22 (2000) 41–47, doi:http://dx.doi.org/10.1520/CCA10462J.
[47] M.A.T.M. Broekmans, Deleterious reactions of aggregate with alkalis in concrete, Rev. Mineral. Geochemistry. (2012), doi:http://dx.doi.org/10.2138/rmg.2012.74.7.
[48] A. Sičáková, M. Špak, The effect of a high amount of micro-fillers on the long-term properties of concrete, Materials (Basel). (2019), doi:http://dx.doi.org/10.3390/ma12203421.
[49] B. Kerkhoff, Effects of Substances on Concrete and Guide to Protective Treatment, Portl. Cem. Assoc. (2007) 36 pp.
[50] BS EN 196-2:2013 - Method of testing cement. Chemical analysis of cement, (n.d.). https://shop.bsigroup.com/ProductDetail/?pid=000000000030263184 (accessed July 31, 2020).
[51] H.T. Le, K. Siewert, H.-M. Ludwig, Alkali silica reaction in mortar formulated from self-compacting high performance concrete containing rice husk ash, Constr. Build. Mater. 88 (2015) 10–19, doi:http://dx.doi.org/10.1016/j.conbuildmat.2015.04.005.
[52] BS EN 13263-1:2005+A1:2009 - Silica fume for concrete. Definitions, requirements and conformity criteria, (n.d.). https://shop.bsigroup.com/ProductDetail?pid=000000000030182182 (accessed July 31, 2020).
[53] BS EN 206:2013+A1:2016 Concrete. Specification, performance, production and conformity - European Standards, (n.d.). https://www.en-standard.eu/bs-en-206-2013-a1-2016-concrete-specification-performance-production-and-conformity/?gclid=CjwKCAjw34n5BRA9EiwA2u9k31XxnXp9PeQMl2s9C35wMNqoSiAM8Ux3ZWbVKoqFzZSa6TR02JTRIRoCkn8QAvD_BwE (accessed July 31, 2020).
[54] Scott M Schlorholtz, ALKALI CONTENT OF FLY ASH: MEASURING AND TESTING STRATEGIES FOR COMPLIANCE Final Report, (2015) .
[55] S. Tsimas, A. Moutsatsou-Tsima, High-calcium fly ash as the fourth constituent in concrete: Problems, solutions and perspectives, Cem. Concr. Compos. 27 (2005) 231–237, doi:http://dx.doi.org/10.1016/j.cemconcomp.2004.02.012.