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Alkali-activated materials obtained from asphalt fillers and fluorescent lamps urban and industrial wastes

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Abstract

Alkali-activated materials, which some authors often call geopolymers, can be described as inorganic solids that form three-dimensional networks with molecular structure similar to organic polymers, and are able to combine qualities similar to cements with those of traditional ceramics and zeolites.

The polymerisation reaction takes place between solid aluminosilicate powders and alkaline solutions at low temperature and therefore this process is classified as eco-efficient. In addition, this process allows the recycling of a large variety of amorphous aluminosilicate waste materials, which makes it very attractive from the environmental point of view.

In this work, alkaline activated materials have been prepared using exclusively industrial and urban wastes to replace both, the aluminosilicate powder (from asphalt fillers and fluorescent lamps wastes) and the alkaline activator (from aluminium manufacturing industry). The materials obtained have been fully characterised. A mineralogical and microstructural study of these materials was conducted by FTIR, XRD, and ESEM-EDX. Moreover, it has been

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determined their bulk density, strength resistance, water absorption and leaching tests,
confirming their suitability for being used as urban pavement.
Keywords: alkali-activated materials; industrial and urban wastes; urban pavement.

1. Introduction

In recent years, the European Commission (EC) has launched a series of initiatives to promote the transition from the current linear economy model (to make – to use – to throw away, implemented in most activities) to a circular model, whose main objectives are: to optimise the use of resources and to avoid and / or to minimise the generation of waste, that is to reduce the generation of industrial waste. In addition to that, the objectives and targets set in European legislation have been key drivers to improve waste management, stimulate innovation in recycling, limit the use of landfilling, and create incentives to change consumer behaviour. If the waste materials are re-manufactured, reused and recycled, and if one industry's waste becomes another's raw material, it will be possible to move to a more circular economy where waste materials are eliminated and resources are used in an efficient and sustainable way (COM (2015) 614 final, 2015; COM (2017) 33 final, 2017).

Alkaline activation is a process in which an aluminosilicate powder is mixed with an alkaline activator to give rise to a mass with the ability to set and harden in a short period of time. As a product of the reaction, a compact material with cementing properties and high mechanical strength is obtained. Alkali-activated materials are formed as a consequence of the polymerisation of simple tetrahedral silicon and aluminium units. The chemical process for the formation of the alkali-activated low calcium materials such as fly ash and metakaolin consists of a first stage of dissolution of the raw materials in the alkaline solution to form inorganic monomers, and a second stage of polycondensation of these monomers to form polymeric structures of oxides in three-dimensional networks (Buchwald et al., 2009). Both steps occur at room temperature or at temperatures below 200 °C, so alkaline activation is considered an eco-efficient or sustainable process.

It is important to note that in the alkaline activation process the thermal stage is eliminated with respect to concrete or ceramic materials manufacturing, resulting in a significant carbon dioxide emissions reduction. Nowadays, in the traditional process, it is necessary to treat the raw materials at 1400-1500 °C in order to obtain the clinker, which is essential in most of the cements and therefore in concretes. On their behalf, ceramic tiles are produced at 1100-1200 °C. On the contrary, the alkali activation process requires low temperatures ($T < 200$ °C), offering considerable energy savings compared to the traditional process of manufacturing urban pavements. Moreover, during the thermal stage, all volatile compounds from the raw materials evolve what make difficult the recycling of some types of waste. Thus, by eliminating

the thermal stage, not only emissions of carbon dioxide will be reduced, but also emissions of sulphur, fluorine, chlorine and heavy metals compounds. This makes alkaline activation an attractive technology from an environmental point of view.

There is a large quantity of literature about the use of waste to replace aluminosilicate raw materials in the alkaline activation process. Much of the work reported in the literature has been based on the study of fly ashes from thermoelectric power plants (Criado et al., 2012; Fernández-Jiménez et al., 2008; Görhan and Kürklü, 2014; Palomo et al., 1999). This kind of fly ash particles is generally spherical in shape, though it is not necessarily homogeneous, so that the fly ash is constituted by a major vitreous phase and by some minor crystalline phases such as quartz, mullite, hematite, magnetite and some CaO and TiO₂ (Fernández-Jiménez and Palomo, 2003; Ryu et al., 2013; Soutsos et al., 2016). The chemical composition of fly ash is silicon-silica, aluminium-alumina, and iron oxides. The amount of crystalline and glassy phase depends largely on the combustion and gasification process used at each power plant. When the maximum temperature of the combustion process is above 1200 °C and the cooling time is short, the ash produced is mostly glassy phase material. Alkali-activated materials prepared by fly ashes exhibit good strength values; the activation of fly ash leads to the formation of alkaline aluminosilicate hydrate gel, main reaction product, which is the main responsible for the mechanical properties in the resulting material (Fernández-Jiménez et al., 2008).

To a lesser extent, there is also literature about the use of fly ash and bottom ash from the incineration of municipal urban solid waste (MSW) (Lancellotti et al., 2010; Zheng et al., 2011). Ashes from biomass (Shearer et al., 2016) have also been studied, as well as other amorphous residues containing silicon and aluminium in their structure (Frías et al., 2012; Hwang and Huynh, 2015; Mijarsh et al., 2015; Santa et al., 2013; Tchadjié et al., 2016; Tchakoute et al., 2013).

In addition, there are very few studies on the use of waste materials for replacing alkaline activators. Alkaline solutions able to interact with aluminosilicates include: alkaline or alkaline-earth hydroxides (ROH, R(OH)₂), weak acid salts (R₂CO₃, R₂S, RF), strong acid salts (Na₂SO₄, CaSO₄·2H₂O) and R₂O(n)SiO₂-type siliceous salts, where R is an alkaline ion such as Na, K or Li. From the standpoint of end-product strength and other properties, the most effective of these activators are a mixture of sodium hydroxide and sodium silicate hydrate (waterglass). Glass waste and rice husk ash have been successful demonstrated to be a viable

substitute for the waterglass (Tchakouté et al., 2016; Torres-Carrasco and Puertas, 2015); however, there are no studies about the substitution of sodium hydroxide by a waste material.

In this work, alkali-activated materials have been prepared using exclusively waste materials; neither primary raw materials nor commercial activators have been used. In this way, asphalt fillers and fluorescent lamps waste, that are currently landfilled, have been used as aluminosilicate waste materials. In addition, sodium hydroxide solutions obtained from the aluminium manufacturing industry has been used as alkaline activator.

The starting materials were previously characterised by chemical and mineralogy methods. A deep and detail mineralogical and microstructural characterisation of the different alkali-activated materials were also carried out by infrared spectroscopy (FTIR), X-ray diffractometry (XRD), and environmental scanning electron microscopy (ESEM). Moreover, compacity, mechanical strength, water absorption and leaching tests were carried out to confirm their suitability for their use as urban pavement.

2. Experimental

2.1. Waste materials characterisation

To produce the alkali-activated materials, asphalt fillers waste (A) and fluorescence lamp waste (FL), were used as starting materials. Asphalt fillers, which are an industrial waste, came from the elimination of the fines of the calcareous aggregates used in road paving. Fluorescence lamps, which are an urban waste, were provided by a Spanish waste manager. Both waste materials were milled and sieved to obtain a pulverulent material with a particle size $< 100 \mu\text{m}$ (Figure 1). For this, 100 g of waste material with a solid content of 70% were wet grounded in a planetary alumina ball mill (MILL-2, Gabbrielli, srl, Italy) with distilled water for 25 minutes at 410 rpm. After that, the material was dried in infrared lamps and the dry powder was de-agglomerated in a centrifugal laboratory crusher (Model 10000, Orto Alresa, Spain).

The particle size distribution of the obtained powders was determined by laser diffraction (Mastersizer 2000, Malvern Instruments Ltd, UK) and the chemical composition by wavelength dispersive X-ray fluorescence (Axios, PANalytical, The Netherlands).

Figure 1. Images of (a) original asphalt waste, (b) powder asphalt waste, (c) cut glass of fluorescent lamp waste and (d) powder fluorescent lamp waste.

The activating agent were sodium hydroxide solutions obtained from the cleaning of the moulds used for extruding aluminium parts provided by a Spanish aluminium manufacturing industry.

2.2. Preparation of test specimens

Compositions detailed in table 1 were activated using 8.8M NaOH waste solution with different liquid/solid ratio (l/s), being 0.45 for 100A, 0.6 for 100FL and 0.5 for the other mixtures (87.5A-12.5FL, 75A-25FL and 62.5A-37.5FL). The change in the l/s ratio was conducted to reach a suitable paste viscosity for filling the moulds during shaping.

Compositions were mixed with the alkaline solution for 10 minutes in a mixer with a blade and a bucket speed of 360 and 60 rpm, respectively.

Table 1. Compositions studied (% by weight).

In addition, 75A-25FL mixture was also activated with 9.9M NaOH waste (75A-25FL-2). This new test was carried out to know the effect of a higher concentration of NaOH and dissolved aluminium in the alkaline solution on the mineralogical, microstructural and mechanical performance of the alkali-activated material.

The obtained pastes were shaped in 80 x 20 x 7 mm moulds and subsequently cured in an oven at 85 °C in a saturated water vapour atmosphere for 20 hours. After that, the specimens were demoulded and dried at room temperature for 24 hours before determining their properties.

2.3 Characterisation of the test specimens

The mineralogical and microstructural characterisation were carried out through the following techniques:

- X-ray diffraction, XRD (D2 Phaser, Bruker, Germany), with Cu-K α radiation and a nickel filter. The tests were conducted with a step size of 0.02° and a counting time of 1.1 s/step, from 5° to 60° 2 θ .

- Fourier-transform infrared spectroscopy, FTIR (Model 1600, Perkin Elmer Inc., Belgium). The samples were prepared by mixing 200 mg of KBr and 1 mg of the powered sample. Spectral analysis was performed over the range 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹ (16 scans).

- Environmental scanning electron microscopy, ESEM (TM3030, Hitachi Ltd., Japan) and energy dispersive X-ray microanalysis, EDX (Quantax 70, Bruker, Germany). The acceleration voltage used was 15 kV and for elemental analysis a total of 25 acquisitions were obtained per sample.

The ability of the alkali-activated materials for being used as urban pavement was determined by:

- Bulk density, determined by the mercury immersion method.

- Three point bending strength. Tests were conducted in a mechanical testing machine (CM-C, Hoytom, S.L., Spain) at a constant deformation speed of 5 mm/min.

- Water absorption. Water absorption was calculated by measuring the weight gain underwent by the specimens after being subjected to a vacuum pressure of 91 kPa for 30 minutes. After that, they were immersed in water and remained in water at atmospheric pressure for 15 minutes.

-Leaching tests. There are no regulations on leachate in building materials; that is the reason why they have been followed the criteria and procedures for the acceptance of waste at landfills. Leaching tests were carried out following the procedure described in the standard UNE-EN 12457-2 (UNE-EN 12457-2:2003, 2003). For this 0.045 ± 0.005 kg of sample was stirred in distilled water with a liquid/solid ratio of 10 l/kg. The sample was under stirring for 24 hours and after that, it was filtered. Analysis of elements in the leachate was performed by inductively coupled plasma optical emission spectrometry, ICP-OES (Model 5100, Agilent Technologies, USA), flame atomic absorption spectrophotometry, FAAS (Aanalyst 400, Perkin Elmer Inc., USA) and ionic chromatography, IC (ICS1000, Dionex, USA).

3. Results and discussion

3.1. Waste materials characterisation

The particle size distribution of the ground powders is shown in figure 2. FL particle size is slightly smaller than the one corresponding to A powder, being the average size value 6.8 µm and 11.3 µm, respectively. It should be notice that FL shows a monomodal particle-size distribution while A particle size is bimodal with two maximum peaks at 2.5 and 28.3 µm.

The chemical composition of the powdered waste materials is shown in table 2. Asphalt filler waste was formed mainly by CaO and MgO, coming from carbonates, and heavy metals were not detected. Fluorescence lamp waste came from the cleaning treatment of fluorescence lamps, in which rare earth elements were removed. The waste contained a large amount of SiO₂ and was still contaminated with heavy metals (Table 2), plastic and other elements such as adhesives and resins.

Figure 2. Particle size distributions of A and FL milled powders.

Table 2. Chemical composition of asphalt filler (A) and fluorescence lamp (FL) waste powders, and NaOH waste solution dried at 110 °C, determined by WD-XRF (% by weight).

Table 3 shows the molarities of the different samples of the sodium hydroxide waste which change according to the time that they had been stored in the industry. The molarities increased with the storage time due to the evaporation of the water contained in the tanks. Apart from sodium, NaOH waste solutions contained impurities of aluminium, as it is shown in the chemical analysis (Table 2).

Table 3. Molarity of NaOH waste samples with different the storage times.

3.2. Mineralogical and microstructural characterisation

3.2.1. X-ray diffraction (XRD)

Figure 3(a) shows the XRD pattern of both raw materials. FL waste consisted of an amorphous phase, according to the wide and diffusive reflection in the interval of 15-35° angles 2θ. XRD analysis of A waste revealed quite different crystalline phases such as calcite (CaCO₃) (PDF # 86-2334), dolomite (CaMg(CO₃)₂) (PDF # 11-0078), muscovite (KAl₂(Si₃AlO₁₀)(OH)₂) (PDF # 01-1098) and quartz (SiO₂) (PDF # 85-0865). These crystalline phases are the typical ones used as raw materials in the production of the asphalt (Jelić et al., 2018).

Figure 3. XRD patterns of (a) the starting materials and (b) the activated materials.

In the alkali-activated pure materials (100FL and 100A), XRD patterns showed differences in the identified phases with respect to the anhydrous raw materials. In 100FL, the halo attributed to the amorphous phase in the initial fluorescence lamp waste shifted to slightly higher angular values ($2\theta = 21-38^\circ$), indicating the formation of a calcium silicate hydrated (C-S-H) with Na in its structure. In 100A, phases identified were pirssonite (Na₂Ca(CO₃)₂·2H₂O) (PDF # 24-1065), hydrotalcite ((Mg_{0.667}Al_{0.33})(OH)₂(CO₃)_{0.137}(H₂O)_{0.5}) (PDF # 89-0460) and brucite (Mg(OH)₂). The crystalline phases (calcite, quartz, muscovite and dolomite) were also detected, while that the three formers remained unaltered with the activation, the amount of dolomite decreased.

XRD patterns for the mixtures (87.5A-12.5FL, 75A-25FL and 62.5A-37.5FL) are shown in figure 3(b). Limited amorphicity was observed and the new crystalline phases detected were the same that those formed in 100A next to thermonatrite (Na₂CO₃·H₂O) (PDF # 08-0448). The formation of single and double sodium carbonate was favoured due to the atmospheric

carbonation, CO₂ reacts with Na ions supplied by the alkaline solution (Komnitsas et al., 2015). In addition, the amount of thermonatrite (Na₂CO₃.H₂O) increased with the presence of a large percentage of FL in the samples, to the detriment of pirssonite (Na₂Ca(CO₃)₂.2H₂O) and brucite (Mg(OH)₂). Fluorescence lamp waste presented a higher amount of Na₂O in its chemical composition than asphalt fillers waste and the formation of single sodium carbonate was favoured.

In 75A-25FL sample activated with richer-Al NaOH solution (75A-25FL-2), the diffractogram presented clear differences with respect to its analogue, new phases were identified such as an unnamed zeolite (Na₈Al₆Si₆O₂₄(CO₃)_{0.5}(OH).3H₂O) (PDF # 49-0757) and hydrogrossularite katoite (Ca₃Al₂(SiO₄)_{1.5}(OH)₆ Ca₃Al₂(OH)₁₂, calcium aluminium garnet-) (PDF # 38-368 02-1124), while that pirssonite and brucite were not formed. Therefore, it was clearly observed that the presence of a higher amount of aluminium promoted the formation of aluminium compounds. In this mixture, the amount of dolomite was higher than calcite.

3.2.2. Fourier-transform infrared spectroscopy (FTIR)

Figure 4(a) shows the infrared spectroscopic results for the fluorescence lamp waste and asphalt fillers waste. The respective spectra band assignments are summarised in table 4. In fluorescence lamp waste spectrum, the bands detected in the region of 3450 cm⁻¹ (peak 4) and around 1650 cm⁻¹ (peak 17) were assigned to stretching and bending H-O-H vibration of water molecules. The peaks around 2920 and 2850 cm⁻¹ (peaks 9,10) were typical C-H stretching vibrations in aliphatic chains of plastic, adhesives or resins (Silverstein et al., 2014). The small band at 1430 cm⁻¹ (peak 18) was attributed to asymmetric stretching vibration of CO₃²⁻ groups. Two main very wide and intense bands characteristics of the internal vibrations in TO₄ tetrahedra (T= Si or Al) were observed. The band at 1040 cm⁻¹ (peak 21) was associated with T-O bond asymmetric stretching vibration, ν₃ (Si-O), of the amorphous phase of the fluorescence lamp waste, and the band at 472 cm⁻¹ (peak 34), corresponded to T-O bond internal deformation or bending vibration, ν₄ (O-Si-O) (Gadsden, 1975). The band at 775 cm⁻¹ (peak 25) was attributed to vibrations of AlO₄⁻ tetrahedral groups (Gadsden, 1975).

Figure 4. FTIR spectra of (a) the starting materials and (b) the activated materials.

Table 4. Bands on the FTIR spectra of the starting materials and the activated materials.

The FTIR spectrum of asphalt fillers waste showed a small peak at 3697 cm⁻¹ (peak 1) due to hydroxyl stretching vibration in brucite (Frost and Klopogge, 1999). The bands at 3621, 3431, 1028, 534 and 475 cm⁻¹ (peaks 3, 5, 22, 32 and 33) were assigned to muscovite (Vaculikova and Plevova, 2005). The bands at 2973, 2957, 2876, 2513, 1799, 1433, 875, 728 and 712 cm⁻¹ (peaks 11, 12, 13, 14, 15, 18, 23, 27 and 28) were attributed to the modes of CO₃²⁻ in CaCO₃ (Vaculikova and Plevova, 2005). The infrared spectra of calcite and dolomite were practically identical due to the similarity of the atomic structure of these minerals.

Figure 4(b) shows the infrared spectra of all activated samples. Table 4 lists the band attribution for all the spectra shown in this figure. In 100FL spectrum, a series of new bands were observed at 2966, 1728, 1274 and 755 cm⁻¹, all of them belonged to vibration bands of organic compounds. The triplet of signals (2966, 2919, 2851 cm⁻¹, peaks 8, 9 and 10) were ascribed to asymmetric stretching of CH₃ groups, asymmetric stretching of CH₂ groups and symmetric stretching of CH₃ groups (Silverstein et al., 2014), the peak at 1728 cm⁻¹ (peak 16) was assigned to the asymmetric stretching of C=O bond (Silverstein et al., 2014). The bands at 1274 and 755 cm⁻¹ (peak 19 and 26) were assigned to bending vibrations of Si-C bonds (Silverstein et al., 2014). The bands at 1462 and 867 cm⁻¹ (peak 18 and 23) were due to atmospheric carbonation and were attributed to asymmetric stretching vibrations and out-of-plane deformation, respectively, of CO₃²⁻ groups. In the activated fluorescence lamp waste, the position of the main band of T-O bond asymmetric stretching was shifted to lower wavenumbers (1002 cm⁻¹, peak 21), confirming the formation of the calcium silicate hydrated gel (Hajimohammadi et al., 2011). The appearance of band at lower wavenumbers was due to the formation of Si-O-T bonds with an increase in the length and/or angle. In addition, this spectrum showed other peaks at around 634 cm⁻¹ (Si-O-Si bending vibration, peak 30) and 456 cm⁻¹ (O-Si-O vibrations, peak 34), likewise typical of C-S-H gels (García-Lodeiro et al., 2008).

In 100A spectrum, the peaks associated to muscovite and calcite/dolomite compounds were still observed and the intensity of the peak at 3697 cm⁻¹ (peak 1) was increased, indicating the formation of a higher amount of brucite, also observed through XRD. Moreover, new set of peaks were detected at 3227, 3075, 1069 and 655 cm⁻¹ (peaks 6, 7, 20 and 29), they were assigned to the presence of pirssonite (Frost and Dickfos, 2007). This compound has other bands at 875 and 712 cm⁻¹ (peaks 23 and 28), which overlapped with the vibrations bands of CO₃²⁻ groups of calcite (Frost and Dickfos, 2007). The asymmetric stretching band of CO₃²⁻ group (peak 18) presented two small peaks, indicating there was a mixture of carbonate compounds in the sample, such as pirssonite, calcite and dolomite.

The 87.5A-12.5FL, 75A-25FL and 62.5A-37.5FL spectra showed the two main bands characteristics of the internal vibrations in TO_4 tetrahedra ($\text{T}=\text{Si}$ or Al) of the calcium silicate hydrated gel. The first band (peak 21) appeared at 1017 cm^{-1} for 87.5A-12.5FL, 75A-25FL mixtures and at 1002 cm^{-1} for 62.5A-37.5FL mixture. The shift of the position of the band at lower wavenumbers could be due to an increase in the content of non-bridging oxygens or an increase in the extent of Al incorporation into the gel structure (Hajimohammadi et al., 2011). In 62.5A-37.5FL sample, where the percentage of SiO_2 was higher, the appearance of band at higher wavenumbers could be expected, but this did not occur and therefore, an increase in non-bridging oxygens could have taken place. In addition, the intensity of this band was the highest in 62.5A-37.5FL sample, higher amount of main reaction product was formed. The second band appeared at 456 cm^{-1} (peak 34), increasing its intensity with the amount of fluorescence lamp waste in the sample, coming to mask the peak at 475 cm^{-1} (peak 33) associated to muscovite. The intensity of peaks ascribed to vibrations generated by brucite and pirssonite also decreased with the increase of content of fluorescence lamp waste in the mixture, in agreement with the XRD results. The band in the range of $1486\text{--}1428\text{ cm}^{-1}$ (peak 18) showed clearly two peaks in the spectrum of 87.5A-12.5FL sample, associated to the modes of CO_3^{2-} in pirssonite (1486 cm^{-1}) and in calcite (1428 cm^{-1}), while this band only presented a peak in the spectrum of 62.5A-37.5FL mixture (1450 cm^{-1}), ascribed to calcite. Thermonatrite, sodium carbonate, was not detected in the FTIR spectra because its main vibration bands overlapped with the vibration modes of calcite or dolomite.

The infrared spectrum for 75A-25FL-2 sample is reproduced in figure 4(b). The most relevant finding in this spectrum was the shift observed in the T-O band, recorded to 1007 cm^{-1} (peak 21). This shift was indicated of changes in the Si/Al ratio in the chief reaction product, in this case an enrichment of gel in aluminium was favoured. The position of this band in the analogous sample activated with poorer-Al NaOH solution waste was at 1017 cm^{-1} , where a lower extent of Al substitution in the C-S-H gel took place. FTIR analysis confirmed the presence of the main vibration types of katoite hydrogrossular: 3664 (O-H stretching vibration, peak 2), 796 and 537 cm^{-1} (two lattice vibrations, peaks 24 and 31) (Kolesov and Geiger, 2005), and the absence of vibrations of pirssonite and brucite.

3.2.3. Environmental scanning electron microscopy (ESEM) and energy dispersive X-ray microanalysis (EDX)

Figure 5 shows SEM images of 100FL and 100A samples. The matrix of 100FL was totally smooth with a uniform microstructure, similar to a glass, in which some microcracks were observed. These cracks are due to the high shrinkage of silica-rich samples ($\text{SiO}_2=67.8\%$) and they have also been observed when activating ceramic frits with a high quantity of silica in their composition (information not presented in this work) (Arulrajah et al., 2016; Garcia-Lodeiro et al., 2014; Kourtí et al., 2011). The matrix of 100A presented a greater degree of heterogeneity with undissolved fines particles such as calcite, dolomite and quartz, which agreed with the worst mechanical performance reported for this mixture (see 3.3 section). In this case, cracks do not appear due to the low silica content in the matrix ($\text{SiO}_2=7.3\%$). The EDS analysis (Table 5) and the EDS maps (not shown) showed the main elements present in both matrix were Si, Na, Al, Ca, Mg and O and K, which are related to the elemental composition of starting material and the alkaline activator. Si and Na were the main components detected in 100FL specimen, while Ca was found in smaller quantities. 100A specimen showed high contents of Ca and Na and a low content of Si.

Figure 5. SEM images (2000x) of the alkali-activated samples: (a) 100FL, (b) 100A, (c) 87.5A-12.5FL, (d) 75A-25FL, (e) 63.5A-37.5FL and (f) 75A-25FL-2.

Table 5. Energy dispersive X-ray spectroscopy (EDS) data of the different gels in the samples.

The microstructure of 87.5A-12.5FL, 75A-25FL and 62.5A-37.5FL specimens is shown in figure 5(c), (d) and (e). It was observed a certain degree of heterogeneity, with larges particles of unreacted asphalt filler particles surrounded by the alkali-activation reaction products (dark area). An increase of content of FL waste leaded to a denser and more compact reaction product, what impact on the bending strength, as discussed later. It should be noted that when A waste is added, cracks do not appear probably due to the lower shrinkage during the curing stage. In these samples, the EDS maps showed Si, Na and Ca as the main components. As an example, figure 6 shows the EDS map for 75A-25FL sample. Four distinctive areas could be identified in this image, Ca-rich (calcite), Ca and Mg-rich (dolomite), Si and O-rich (quartz) and a homogeneous matrix containing Si, Al, Ca and Na, consistent with a gel of calcium silicate hydrate with Al and Na in its structure, which agreed with the results obtained by XRD and FTIR.

Figure 6. EDS maps showing the microstructure of 75A-25FL sample and partitioning of key elements.

SEM image of 75A-25FL-2 (Figure 5(f)), prepared with high NaOH molarity (9.9 M), presented a heterogeneous microstructure, similar to that of the specimen 75A-25FL. However, the microstructure of the reaction product seemed different, in this sample it had less compaction and continuity due to the fact that the NaOH waste solution used in this composition had a high quantity of aluminium dissolved in. In addition, Si/Al and Na/Al ratios for this sample were lower than those obtained for 75A-25FL specimen (Table 5) and it is because the largest amount of dissolved aluminium. Although, a high content of Al, which is one of the main elements required for the formation of aluminosilicate bonds, was detected in 75A-25FL-2 sample, the final strength of the specimens did not change markedly (see 3.3 section).

3.3. Aspect of the alkali-activated samples, bulk density, bending strength and water absorption

Figure 7 shows the images of the specimens before characterisation. 100FL are full of cracks, some of them comes through the piece, breaking it (Figure 7(a)). 100A have an irregular colour, but they are entire and their edges depict a complete parallelepiped (Figure 7(b)). When FL is added to the composition (Figure 7(c), (d) and (e)), the brown colour is more homogeneous; however, by adding more amount of FL (Figure 7(e)), which is a white powder, the brown colour becomes less intense. Finally, the samples prepared with higher-molarity and richer-Al NaOH waste (Figure 7(f)) change the colour completely, possibly due to the formation of new aluminium compounds (see XRD pattern in figure 3(b) and FTIR spectrum in figure 4(b)).

Figure 7. Specimens' photographs: (a) 100FL, (b) 100A, (c) 87.5A-12.5FL, (d) 75A-25FL, (e) 63.5A-37.5FL and (f) 75A-25FL-2.

Figure 78 shows the results of bulk density and bending strength of 10 tested specimens. The evolution of both properties with the FL content is quite similar, with a maximum around the composition with 25% of FL. The data of the composition 100FL is not included due to the presence of cracks in the test specimens, which are the result of an excessive shrinkage of the test specimens during the curing together with their stuck to the mould.

Regarding the bending strength, data for 100A (Figure 87) was quite low mainly due to the small silica content (7.3%) in the asphalt fillers waste, since a certain quantity of silica is

required to form the gel. When FL was added to the composition, bulk density and bending strength of the compositions raised due to the increase of silica in the network of the activated material. The increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio has positive effects on the strength since Si–O–Si bonds are stronger than Si–O–Al and Al–O–Al bonds, it is expected that the strength of the activated mixtures will increase (Bobirić et al., 2015; Novais et al., 2016). This trend reached a maximum (around 75A-25FL), and then both properties, apparent density and mechanical resistance, decreased as it is observed in figure 78. This decrease in both parameters could be due to an excess of the amount of silica required, in agreement with the lower activation degree presented in high silica glasses (Arulrajah et al., 2016; Garcia-Lodeiro et al., 2014; Kourti et al., 2011).

Figure 78. Bulk density and bending strength vs FL addition.

In the case of the sample activated with higher-molarity and richer-Al NaOH waste (75A-25FL-2), although the higher NaOH concentration is more effective in dissolving aluminosilicate particles and the higher Al dissolved in the NaOH waste promotes the formation of aluminium compounds (see XRD pattern in figure 3(b) and FTIR spectrum in figure 4(b)), the bending strength values did not change noticeably (Table 6).

Table 6. Bulk density and mechanical bending strength of the same composition activated with different NaOH waste solutions.

Table 7 shows the minimum bending strength requirements for the different performance classes corresponding to concrete tiles used as urban pavement. Comparing the bending strength data of the compositions tested with these data in Table 6, it is observed that the specimens prepared with the wastes showed higher values than the ones required by the standard. That is the reason why these alkali-activated materials could be used for urban paving.

Table 7. Performance classes and marking of concrete tiles for urban pavement, according to standards UNE-EN 1339:2004 and UNE 127339:2007 (UNE-EN 1339 2004; UNE 127339:2007, 2007).

Regarding the water absorption, these values are ranged between 15 and 25% (Table 8), taking into account that samples with higher mechanical strengths (75A-25FL and 75A-25FL-2) lead to samples with lower water absorption, and vice versa. Note that water absorption could not be determined in 100FL specimens due to the cracks.

Table 8. Water absorption of the alkali-activated samples.

3.4. Leachability test

Leachability test were carried out with the sample that provided the highest values of bending strength, 75A-25FL.

Comparing the list of elements described in the guidelines set out in the Council Decision 2003/33/EC of 19 December 2002 and the Article 16 and Annex II to Directive 1999/31/CEE (Council Decision 2003/33/EC, 2003) (see 2.3. section) with the elements contained in the starting waste materials (Table 2), the elements analysed in the leachate were: barium, lead and sulphates.

All of them (Ba, Pb and SO_4^{2-}) come from FL waste, since their quantities in A and NaOH wastes are lower than 0.01% (Table 2). The comparison of BaO, PbO and S content in the starting composition with the values determined in the leachate (Table 98), allows to conclude that almost the whole amount (>99.9 %) of Ba and Pb have been encapsulated in the network of the alkali-activated material. In the case of sulphate, the amount retained was a little lower: 539 mg/kg in the leachate with respect to 2400 mg/kg in the FL starting powder; that is, 77.5%.

Table 98 shows the maximum limits allowed by the regulation regarding the type of waste and the results obtained for sample 75A-25FL. It can be concluded that activated material obtained can be classified as inert.

Table 98. Maximum values allowed for different types of landfill waste and results of the characterised sample. Leaching test according to the standard UNE-EN 12457-2, Part 2 (UNE-EN 12457-2:2003, 2003).

4. Conclusions

This paper deals with alkaline activated materials obtained exclusively with industrial and urban wastes both, for the aluminosilicate solid and the alkaline solution.

The dosage of solid waste and the concentration and composition of alkaline activator play an important role in the mineralogy and microstructure the alkali-activated materials obtained. In this study, an increase of the percentage of fluorescent lamp waste to the detriment of asphalt fines waste in the binders meant the formation of single sodium carbonates and the development of a microstructure denser and more compacted.

The use of an alkaline activator, sodium hydroxide, with a higher concentration and a greater amount of aluminium promoted the formation of crystalline aluminium compounds and the enrichment in aluminium of the calcium silicate hydrate gel. The microstructure of the matrix had less compaction and continuity, but its Al content was high, favouring the formation of aluminosilicate bonds. However, this content was not enough to improve the bending strength.

When FL is added to A composition, bending strength raises due to the increase of silica in the network of the activated material, reaching a maximum in 75A-25FL composition; in this instance, bending strength is 5.6 times higher than the one measured in specimens without FL (100A). Bending strength values of the alkaline activated products obtained point out that they can be used for urban paving. In addition, leaching tests show the effectiveness of this process for retain heavy metals in the network formed.

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Prof. Dr. Jiří Jaromír Klemesš,
Editor-in-Chief, *Journal of Cleaner Production*
Brno University of Technology (VUT Brno),
Antonínská 548/1, Brno, Czech Republic

Re: Manuscript submission for Journal of Cleaner Production

Dear Professor Klemesš,

Accompanying this letter is a manuscript submitted for publication in *Journal of Cleaner Production*. This manuscript is written in a Regular Article, and is entitled “Alkali-activated materials obtained from industrial wastes”.

This manuscript represents an important role in the reutilisation and the viability of industrial wastes (fluorescence lamp, asphalt fine wastes and recycled NaOH) in the construction field. Here, we carried out a deep and exhaustive characterisation of the raw materials and the new cementitious materials and their suitability for being used as urban pavement, both from mechanical and environmental points of view.

This work is both scientifically novel and industrially important, and is thus ideally suited to publication in *Journal of Cleaner Production*, as it brings a new application of industrial wastes as urban pavement.

I am pleased to confirm that the work described has not published before; it is not under consideration for publication anywhere else; and publication has been approved by all co-authors and the responsible authorities at the institutes where the work has been carried out.

Three potential referees, all experts in immobilisation and treatment of wastes in alkali cements:

- Christopher R. Cheeseman, Department of Civil and Environmental Engineering, Imperial College London, London SW7 2AZ, UK, email: c.cheeseman@imperial.ac.uk
- Cristina Leonelli, Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università di Modena e Reggio Emilia, Via Vignolese 905, 41100 Modena, Italy. Email: cristina.leonelli@unimore.it
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Yours sincerely,

Maria Criado

Graphical Abstract

Graphical abstract. Process’ diagram

Highlights.

- Lamp, asphalt fine and recycled NaOH were used to produce alkaline cements.
- Bending strength values demonstrated that they can be used as urban pavement.
- Leaching tests showed the effectiveness of this process for retain heavy metals.

FIGURE CAPTIONS

Figure 1. Images of (a) original asphalt waste, (b) powder asphalt waste, (c) cut glass of fluorescent lamp waste and (c) powder fluorescent lamp waste.

Figure 2. Particle size distributions of A and FL milled powders.

Figure 3. XRD patterns of (a) the starting materials and (b) the activated materials.

Figure 4. FTIR spectra of (a) the starting materials and (b) the activated materials.

Figure 5. SEM images (2000x) of the alkali activated samples: (a) 100FL, (b) 100A, (c) 87.5A-12.5FL, (d) 75A-25FL, (e) 63.5A-37.5FL and (f) 75A-25FL-2.

Figure 6. EDS maps showing the microstructure of 75A-25FL sample and partitioning of key elements.

Figure 7. Specimens' photographs: (a) 100FL, (b) 100A, (c) 87.5A-12.5FL, (d) 75A-25FL, (e) 63.5A-37.5FL and (f) 75A-25FL-2.

Figure 87. Bulk density and bending strength vs FL addition.

Figure 1.

Figure 2.

Figure 4.

Figure 5.

BSE

Ca-KA

Mg-K

Na-KA

Al-K

Si-KA

Figure 6.

Figure 7.

Figure 87.

TABLES

- Table 1. Compositions studied (% by weight).
- Table 2. Chemical composition of asphalt filler (A) and fluorescence lamp (FL) waste powders, and NaOH waste solution dried at 110 °C, determined by WD-XRF (% by weight).
- Table 3. NaOH waste molarity according to the storage time.
- Table 4. Bands on the FTIR spectra of the starting materials and the activated materials.
- Table 5. Energy dispersive x-ray spectroscopy (EDS) data of the different gels in the samples.
- Table 6. Bulk density and mechanical bending strength of the same composition activated with different NaOH waste solutions.
- Table 7. Performance classes and marking of concrete tiles for urban pavement, according to standards UNE-EN 1339:2004 and UNE 127339:2007 (UNE-EN 1339 2004; UNE 127339:2007, 2007).
- Table 8. Water absorption of the alkali-activated samples.
- Table 9. Maximum values allowed for different types of landfill waste and results of the characterised sample. Leaching test according to the standard UNE-EN 12457-2, Part 2 (UNE-EN 12457-2:2003, 2003).

Table 1. Compositions studied (% by weight)

Composition	100A	100FL	87.5A- 12.5FL	75A-25FL	62.5A- 37.5FL
A	100	-	87.5	75	62.5
FL	-	100	12.5	25	37.5

Table 2. Chemical composition of asphalt filler (A) and fluorescence lamp (FL) waste powders, and NaOH waste solution dried at 110 °C, determined by WD-XRF (% by weight).

	SiO ₂	Al ₂ O ₃	⁽¹⁾ B ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	ZrO ₂	BaO	⁽²⁾ Li ₂ O	PbO	ZnO	HfO ₂	P ₂ O ₅	SrO	MnO	S	⁽³⁾ LoI
A	7.3	3.4	-	1.0	35.4	10.8	0.10	0.64	0.11	<0.01	<0.01	-	<0.01	<0.01	<0.01	0.06	<0.01	0.03	<0.01	41.1
FL	67.8	2.1	0.85	0.16	3.90	2.51	16.0	2.15	0.04	0.02	1.37	0.03	0.39	<0.01	<0.01	0.04	0.13	<0.01	0.08	2.47
NaOH	1.5	31.1	-	0.02	0.03	<0.01	39.4	0.20	<0.01	<0.01	<0.01	-	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	12.2

⁽¹⁾B₂O₃ has not been determined by WD-XRF, it has been determined by potentiometry

⁽²⁾Li₂O has not been determined by WD-XRF, it has been determined by FAAS

⁽³⁾LoI: loss on ignition, 900 °C

Table 3. NaOH waste molarity according to the storage time.

Time (days)	NaOH molarity (M)
1	7.2
60	7.5
365	8.8

Table 4. Bands on the FTIR spectra of the starting materials and the activated materials.

Peak	Wavenumber (cm ⁻¹)	Assignment
1	3697	O-H stretching vibration in brucite
2	3664	O-H stretching vibration in hydrogrossular
3	3621	O-H stretching vibration in muscovite
4	3437	H-O-H stretching vibration in water
5	3431	Muscovite band
6	3227	Pirssonite band
7	3075	Pirssonite band
8	2966	Asymmetric stretching of CH ₃ groups
9	2919	Asymmetric stretching of CH ₂ groups
10	2851	Symmetric stretching of CH ₃ groups
11	2973	Calcite band
12	2957	Calcite band
13	2876	Calcite band
14	2513	Calcite band
15	1799	Calcite band
16	1728	Asymmetric stretching of C=O bond
17	1641	H-O-H bending vibration in water
18	1482-1428	Asymmetric stretching vibrations of CO ₃ ²⁻ groups (calcite, dolomite, pirssonite, thermonadite)
19	1274	Bending vibration of Si-C bond
20	1069	Pirssonite band
21	1040	Asymmetric stretching of T-O bond (T=Si or Al) in anhydrous fluorescence lamp waste
	1017-102	Asymmetric stretching of T-O bond (T=Si or Al) in gel
22	1028	Muscovite band
23	875-867	Out-of-plane bending of CO ₃ ²⁻ groups (calcite, dolomite, pirssonite, thermonadite)
24	796	Hydrogrossular band
25	775	Vibrations of AlO ₄ ⁻ tetrahedral groups

26	755	Bending vibration of Si-C bond
27	728	Calcite band
28	712	In-of-plane bending of CO ₃ ²⁻ groups
29	655	Pirssonite band
30	634	Bending vibration of Si-O-Si
31	537	Hydrogrossular band
32	534	Muscovite band
33	475	Muscovite band
34	456	Bending vibration of O-Si-O

Table 5. Energy dispersive x-ray spectroscopy (EDS) data of the different gels in the samples.

Samples	Ratio		
	Si/Al	Na/Al	Ca/Si
100FL	24.90	20.03	0.09
100A	1.74	4.34	3.44
87.5A-12.5FL	5.54	8.02	0.83
75A-25FL	8.24	12.60	0.51
63.5A-37.5FL	16.15	14.31	0.34
75A-25FL-2	2.18	4.07	0.79

Table 6. Bulk density and mechanical bending strength of the same composition activated with different NaOH waste solutions.

Composition	NaOH waste solution molarity (M)	Bulk density (g/cm ³)	Bending strength (MPa)
75A-25FL	8.8	1.888±0.009	6.7±0.6
75A-25FL-2	9.9	1.905±0.006	6.9±0.5

Table 7. Performance classes and marking of concrete tiles for urban pavement, according to standards UNE-EN 1339:2004 and UNE 127339:2007 (UNE-EN 1339 2004; UNE 127339:2007, 2007).

Material		Bending strength (MPa)
Class	Marking	
1	S	≥ 3.5
2	T	≥ 4.0
3	U	≥ 5.0

Table 8. Water absorption of the alkali-activated samples.

Samples	Water absorption (%)
100FL	---
100A	22.5
87.5A-12.5FL	24.3
75A-25FL	17.5
63.5A-37.5FL	22.8
75A-25FL-2	15.4

Table 89. Maximum values allowed for different types of landfill waste and results of the characterised sample. Leaching test according to the standard UNE-EN 12457-2, Part 2 (UNE-EN 12457-2:2003, 2003).

Component	Maximum values allowed (mg·kg ⁻¹)			75A-25FL
	Inert waste	No dangerous waste	Dangerous waste	
Ba	20	100	300	2.5
Pb	0.5	10	50	<0.5
SO ₄ ²⁻	1000	20000	50000	539