OBTAINING ALKALI-ACTIVATED MATERIALS FROM WASTES

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1. ABSTRACT

Alkali-activated materials, which some authors often call geopolymers, may be described as inorganic solids which form three-dimensional networks with a molecular structure analogous to that of organic polymers and with mechanical properties similar to those of ceramic materials.

The polymerization reaction takes place at low temperatures (<200 °C) and thus this process is classified as eco-efficient. Furthermore, this process enables a wide variety of silico-aluminous wastes, which makes it very attractive from the environmental point of view.

In this paper alkali-activated materials have been prepared using wastes only, to replace both the silico-aluminous material and the alkali activator. The materials obtained have been characterised, determining their bulk density, mechanical resistance and leaching, confirming that they are suitable for use in urban paving.

2. INTRODUCTION

Alkali activation is a process in which a particulate silico-aluminous material is mixed with an alkali activator to create a plastic mass capable of setting and hardening in a short period of time. As a product of the reaction a compact material is obtained with cementitious properties and elevated mechanical resistance.

Alkali-activated materials are formed as a result of the polymerization of simple tetrahedral units of silicon and aluminium. The chemical process for the formation of these materials comprises 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 oxide structures in three-dimensional networks [1]. Both steps occur at ambient temperature or a very low temperature ($T < 200$ ºC), thus it is an eco-efficient process.

There is plentiful literature on the use of waste to replace silico-aluminous raw materials. The ones most studied are fly ash from power stations [2], [3], [4], [5] and to a lesser extent fly ash from the incineration of municipal solid wastes [6], [7]. Ash from biomass [8] has also been studied as well as other more amorphous wastes that contain silicon and aluminium in their structure [9], [10], [11], [12], [13], [14]. By contrast, there are very few studies on the use of wastes that act as an alkali activator [15], [16].

In this paper alkali-activated materials have been prepared using only wastes. Thus, besides being able to obviate the firing stage with respect to traditional ceramic materials and considerably reducing carbon dioxide emissions into the atmosphere, an alternative is proposed to the recycling of certain wastes which are currently taken to landfill.

3. EXPERIMENTAL PROCEDURE

Asphalt (A) waste and fluorescent lamps (FL) have been used as silico-aluminous material, and a solution of sodium hydroxide from an aluminium manufacturing company as an alkali activator.

Firstly, silico-aluminous material was ground and sieved in order to obtain a particulate material with a particle size less than 100 µm. Then, this silico-aluminous waste (100A and 100FL) and its mixtures (A-FL) were mixed with the sodium hydroxide (liquid) residue, obtaining a plastic mass that was placed in moulds measuring 80x20x7 mm. This type of forming, which is called formwork, can be done directly after the kneading.

Once the test pieces have been formed, the curing process took place for 20 hours, which was performed by controlling the temperature and relative humidity conditions: 85 ºC and 95%, respectively.

After the curing process, the test pieces were taken from their moulds and were subjected to a drying process at ambient temperature and humidity for 24 hours.

4. RESULTS

4.1. CHARACTERISATION OF WASTES

The chemical analysis of the silico-aluminous wastes are shown in table 1. The asphalt residue used in this experiment came from road surfaces, it is composed mainly of CaO and MgO, and does not contain any heavy metals.

The fluorescent lamp waste came from treating them to recover mercury and other rare earth elements; however, this waste is not yet contaminated with heavy metals (as can be seen from the chemical analysis), plastic and other elements such as adhesives and resins.

	A	FL
SiO_2	7.3	67.8
Al_2O_3	3.4	2.1
Fe_2O_3	1.0	0.16
CaO	35.4	3.90
MgO	10.8	2.51
Na_2O	0.10	16.0
K_2O	0.64	2.15
TiO_2	0.11	0.04
MnO	0.03	<0.01
P_2O_5	0.06	0.04
B_2O_3	-	0.85
ZrO_2	-	0.02
BaO	-	1.37
Li_2O	-	0.03
PbO	-	0.39
ZnO	-	<0.01
HfO_2	-	<0.01
SrO	-	0.13
S	-	0.08
(*)LOI (1000 °C)	41.1	2.47

(*)ppc: loss by calcination

***Table 1**. Chemical analysis of silico-aluminous wastes (%)*

The asphalt waste is characterised by its low proportion of silicon and alumina, responsible for the alkali activation reaction. On the other hand, the fluorescent lamp waste is characterised by a large amount of silicon.

In respect of the waste that is going to act as the alkali activator, it is a sodium hydroxide solution from washing the aluminium extrusion moulds and therefore is contaminated with aluminium.

In table 2 we present the molarity of the waste depending on the time it has been stored. It can be seen that, on increasing the storage time of the waste, the molarity increases due to it being kept in open tanks and part of the water it contains evaporates. Nowadays, this waste is taken to a waste manager, which means a cost for the company.

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

***Table 2**. Molarity of the sodium hydroxide solution depending on the time it has been stored*

4.2. CHARACTERISATION OF ALKALI-ACTIVATED MATERIALS

To prepare alkali-activated materials, larger molarity (8.8M) sodium hydroxide waste has been used.

Table 3 shows the results of bulk density and mechanical resistance to bending of the samples with asphalt waste (100A) and with fluorescent lamp waste (100FL). The mechanical resistance value obtained with the 100A sample is low mainly due to the small proportion of silicon (7.3%) present in the asphalt waste. The test pieces obtained with the fluorescent lamp waste (100FL) presented cracks probably due to the large amount of silicon in the initial waste (67.8%).

In the case of the mixtures of both solid wastes, bulk density and mechanical resistance rise on increasing the amount of FL, mainly due to the increase of silicon in the three-dimensional network of the activated material. This tendency goes through a maximum (25FL) from which both properties, bulk density and mechanical resistance, diminish.

Table 4 shows the minimum requirement of mechanical resistance for the various classes and brands corresponding to the concrete tiles used as urban paving. If we compare the mechanical resistance to bending of the three compositions prepared with mixtures of asphalt and fluorescent lamp with the values shown in table 4, it will be seen that the mechanical resistance values are higher than the values required by the regulations, therefore these materials could be used for urban paving.

Composition	ApD (g/cm^3)	MR$_f$ (MPa)
100A	1.747±0.010	1.2±0.3
100FL	--- (cracks/stuck to the mould)	
87.5A-12.5FL	1.841±0.004	5.6±0.7
75A-25FL	1.888±0.009	6.7±0.6
62.5A-37.5FL	1.851±0.010	6.2±0.6

***Table 3**. bulk density and mechanical resistance to bending of the activated materials*

Material		MR$_f$ (MPa)
Class 1	Brand S	≥ 3.5
Class 2	Brand T	≥ 4.0
Class 3	Brand U	≥ 5.0

***Table 4.** Classes and brands of concrete tiles for urban paving, as in UNE-EN 1339:2004 and UNE 127339:2007 regulations*

In respect of the leaching of the alkali-activated samples, the directives indicated in the Decision of the Council of 19 December 2002 (2003/33/CE) were followed in accordance with article 16 and Annexe II of the Directive 1999/31/CEE, which established a classification of materials depending on their hazard level. Table 5 shows the maximum limits allowed according to type of waste and the results obtained for sample 75A-25FL. It was concluded that the material obtained can be classified as inert.

Component	Maximum permitted values ($mg \cdot kg^{-1}$)			75A-25FL
	Landfill sites for inert waste	Landfill sites for non-hazardous waste	Landfill sites for hazardous waste	
Ba	20	100	300	2.5
Pb	0.5	10	50	<0.5
SO_4^{2-}	1000	20000	50000	539

Table 1. *Maximum permitted values for different types of wastes in landfill sites and results for the sample characterised. Leachate test in accordance with UNE-EN 12457-2, Part 2 test regulation*

5. CONCLUSIONS

Alkali-activated materials have been obtained exclusively using wastes, both for the silico-aluminous material and the alkaline solution.

Mechanical resistance to bending of alkali-activated products indicates that they can be used for urban paving. Furthermore, the leaching tests manifest the effectiveness of this process for fixing heavy metals.

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7. REFERENCES

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