# TOWARDS A LOW-CARBON ECONOMY: ALKALI ACTIVATION TECHNOLOGY FOR OBTAINING CONSTRUCTION MATERIALS

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## 1. INTRODUCTION

On 28 November 2018, the European Commission presented its long-term strategic vision for a prosperous, modern, competitive and climate neutral economy to 2050. The strategy aims to achieve net zero emissions of greenhouse gases by 2050 [1].

In the ceramic sector, the firing stage is the main source of carbon dioxide emissions into the atmosphere. At present, alternatives are being studied to reduce such emissions during this stage. Although some stakeholders support abandoning natural gas-fuelled kilns for electric kilns, it does not seem a feasible economic solution, either at present or in the near future [2]. Therefore, work is in progress to develop ceramic processes with low environmental impact, minimising fossil fuel consumption and always striving to reduce $CO_2$ emissions [3]. In this context, of particular note are alternative gaseous fuels such as biogas or hydrogen, particularly so-called 'green hydrogen', which constitutes a valuable energy vector (it being able to store energy and then gradually release it upon demand), especially in those sectors in which electrification of given processes is not the most efficient option [4].

Other alternatives being studied involve modification of the formulation of ceramic tile and glaze compositions [5], though all these measures will hardly enable the emissions levels targeted by the European Union for 2050 to be reached.

An alternative to reducing emissions, which would entirely change both the starting materials and the manufacturing process, is alkali activation. In alkali activation, the firing stage would be fully suppressed and replaced with a curing stage at temperatures below 100ºC [6]. Eliminating the firing stage promises considerable energy savings. In addition, not only are carbon dioxide emissions reduced, but emissions of sulphur, fluorine, and chlorine compounds, which are released in the firing process of traditional ceramic materials, decrease. Finally, to be noted is the possible use of waste to replace aluminosilicate raw materials [7], whereby, moreover, use of natural resources decreases and waste that usually goes to landfills is recovered. This all makes alkali activation an attractive technology from an environmental viewpoint.

In this study, alkali-activated materials were prepared, exclusively using waste as source of silica and alumina. With a view to extending the variety of wastes that might be used, (activatable) aluminosilicate wastes and other non-activatable wastes, which were introduced as fillers, were tested. It was thus attempted to valorise the use of wastes that are currently being landfilled, such as the waste produced in the ceramic sector itself (fired tile scrap of products with low water absorption). The resulting materials were characterised, it being confirmed that the selected waste was appropriate for manufacturing new porous ceramic materials by alkali activation.

## 2. EXPERIMENTAL

Waste from different industrial sectors, including the ceramic sector, was used as starting material. The wastes were divided into activatable and non-activatable (Table 1). The alkali activator used ($SiO_2/Na_2O$ by weight of 0.2) was prepared by mixing 85% of sodium hydroxide NaOH 10M and 15% of sodium silicate in dissolution with a solids content of 35%.

| Waste | Ref. | Origin | LER code | Type | Appearance (before conditioning) |
|---|---|---|---|---|---|
| Thermal power station fly ashes | CV | Almería (ES) | Non-hazardous 10 01 02 | Activatable |  |
| Fired tile scrap | TC | Toledo (ES) | Inert 10 12 08 | Activatable |  |
| CRT (cathode ray tube) display-screen glass | VP CRT | Albacete (ES) | Non-hazardous 19 12 05 | Activatable |  |
| CRT cone glass | VC CRT | Albacete (ES) | Hazardous 19 12 11* | Activatable |  |
| Solar panel glass | VPS | Albacete (ES) | Non-hazardous 19 12 05 | Activatable |  |
| Construction and demolition | CD | Toledo (ES) | Inert 17 01 07 | Non-activatable |  |
| Clayey sludge | LA | Segovia (ES) | Inert 010412 | Non-activatable |  |

***Table 1.*** *Test wastes*

Representative samples of the wastes were dried and then milled or sieved for use as activatable material (aluminosilicate waste, d<0.2 mm) or non-activatable (non-aluminosilicate waste, d<1 mm).

Two series of compositions were prepared: the first with 100% of each waste and the second with 90% CV and 10% of each CRT glass. Each composition was mixed with the activating solution at a different liquid/solid (l/s) ratio to obtain an appropriate granulate for forming by pressing. After mixing, the granulate was poured into prismatic steel dies (80 x 80 x 160 mm) and pressed at 1 MPa. The test pieces were cured at 85 ºC and 95% relative humidity for 20 hours. They were then kept for 24 hours under ambient conditions prior to characterisation, in which bulk density, open porosity, bending strength, leachate, and microstructure were determined. The Pb leaching test was performed to assure the end product met the relevant criteria to be rated as either inert, non-hazardous, or hazardous.

# 3. RESULTS

## 3.1. CHARACTERISATION OF TEST PIECES OBTAINED FROM ACTIVATABLE WASTES

Table 2 summarises the main results obtained for the test aluminosilicate wastes with a particle size below 0.2 mm. The bulk density (Dap) values depended on the particle size distribution of the waste (residue on 63 μm) and on the amount of gel that formed during the dissolution process, which, on polymerising, filled the voids between the material that had not been activated, therefore not correlating with the l/s ratio. The wastes with the wider distributions (such as VC CRT) packed better and required a smaller amount of activator to obtain the granulate. However, the wastes with a lower amount of small particles (such as CV) packed worse and needed a larger amount of activating solution (Figure 1 left). The values for water absorption (WA) were high in most cases and they correlated well with bulk density values (Figure 1 right). This indicates that this technology provided porous products from the test wastes and that most porosity was open.

The water absorption test also showed that some wastes, such as CRT glass (VP and VC) could not be used alone, as the resulting product was not stable in water and exhibited high solubility. This was because these two glasses had a low alumina content, which significantly weakened the arising structure, leading to an inorganic polymer practically made up of $SiO_2$ and $Na_2O$ that was partially water-soluble. The $Al_2O_3$ content in waste VPS was even lower than that of the two CRT glasses. However, it was stable in water. This behaviour was due to the presence of major amounts of alkaline-earth oxides (Ca and Mg), which reinforced the arising polymer structure, as occurred in glasses [8]. In regard to mechanical strength (MS), this depended on the porosity of the pieces, as well as on the amount of gel that formed, which is why it was not possible to relate this solely to bulk density. However, in general, the MS values obtained were low, if the products are compared with ceramic products, but they were high in relation to cement-based products (terrazzo and tiles with a cementitious basis).

| Waste | l/s | Dap ($g/cm^3$) | WA (%) | MS (MPa) | $K^+$ (%) | $Mg^{2+}$ (%) | Pb (mg/kg) |
|---|---|---|---|---|---|---|---|
| CV | 0.3 | 1.68 ± 0.01 | 12.3 ± 1.0 | 3.4 ± 1.1 | 0.05 | <0.01 | - |
| TC | 0.275 | 1.91 ± 0.03 | 8.5 ± 0.7 | 1.5 ± 0.5 | 0.11 | <0.01 | - |
| VP | 0.25 | 2.07 ± 0.03 | 3.4 ± 1.1* | 6.8 ± 1.3 | 0.89 | <0.01 | 228 |
| VC | 0.20 | 1.80 ± 0.03 | Soluble | 1.8 ± 0.3 | - | - | 6090 |
| VPS | 0.23 | 1.66 ± 0.06 | 15.5 ± 1.2 | 7.0 ± 2.0 | 0.01 | 0.01 | - |

* Partially soluble

***Table 2.*** *Properties of the test pieces prepared with 100% activatable waste*

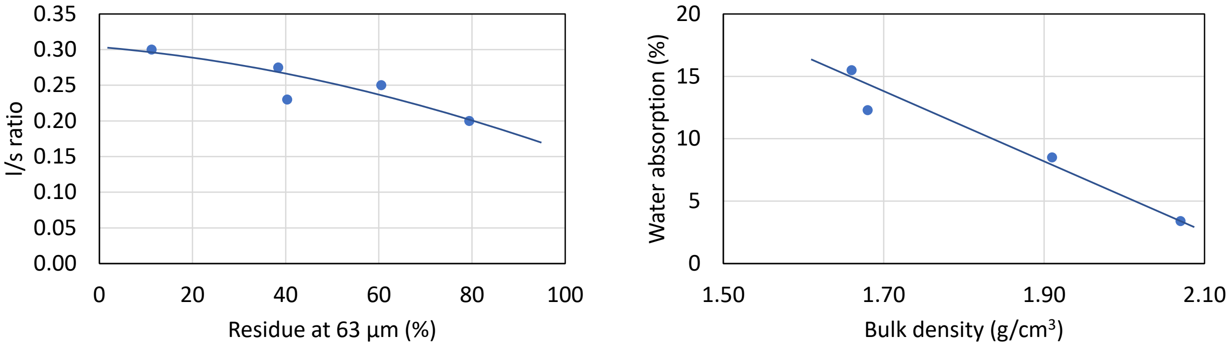

***Figure 1.*** *Evolution of the l/s ratio with waste particle size (left) and of water absorption with bulk density (right)*

Soluble K and Mg content was also determined, as well as that of the Pb leachate for both CRT glasses. As there are no European standards on the determination of soluble K and Mg for ceramic tiles, the existing standard for fired-clay products was used as a reference, as these are the closest ceramic product to tile (UNE-EN 772-5:2002). Except for the pieces corresponding to the CRT glasses, the rest exhibited very low values, and they were classified as S1. With regard to Pb leaching in CRT glasses (UNE-EN 12457-2:2003), the results obtained were very high, owing to the presence of this element in both glasses and to the arising structure being water-soluble, which facilitated Pb leaching. This indicates that these glasses could not be used as sole raw material under the test conditions used.

## 3.2. CHARACTERISATION OF TEST PIECES CONTAINING NON-ACTIVATABLE WASTE

To determine the effect of non-activatable waste on the behaviour and properties of the test pieces, mixtures were prepared in the proportion 90% CV – 10% non-activatable waste (Table 3). This series of compositions included the two CRT glasses with a larger particle size (<2 mm), with a view to decreasing the solubility of the resulting product and lead leaching. The introduction of 10% by weight of non-activatable waste reduced the bulk density values in relation to that of composition CV, and it raised the water absorption values. Both CRT glasses provided similar or even higher mechanical resistance values to those of the CV pieces.

The presence of non-activatable waste did not significantly modify the amount of soluble K and Mg. However, the increase in CRT glass particle size led to a drastic decrease in Pb leaching, not only because its percentage in the composition was low (10%) but also because of the smaller surface area exposed to the alkali solution, which only allowed liberation of the Pb present at the surface of the glass particles. This opens up the possibility of valorising this type of glass with heavy elements in the construction sector.

| Waste | l/s | Dap (g/cm$^3$) | WA (%) | MS (MPa) | K$^+$ (%) | Mg$^{2+}$ (%) | Pb (mg/kg) |
|---|---|---|---|---|---|---|---|
| 100%CV | 0.3 | 1.68 ± 0.01 | 12.3 ± 1.0 | 3.4 ± 1.1 | 0.05 | <0.01 | - |
| VP CRT | 0.25 | 1.60 ± 0.03 | 17.8 ± 1.7 | 4.0 ± 0.5 | 0.05 | <0.01 | <1 |
| VC CRT | 0.2 | 1.55 ± 0.01 | 18.8 ± 0.9 | 3.5 ± 0.8 | - | - | 1.9 |
| CD | 0.2 | 1.48 ± 0.04 | 20.3 ± 1.9 | 2.0 ± 0.2 | 0.03 | <0.01 | - |
| LA | 0.2 | 1.47 ± 0.03 | 21.9 ± 0.8 | 2.0 ± 0.2 | 0.03 | <0.01 | - |

***Table 3.*** *Properties of the test pieces prepared with 90% CV - 10% waste (as filler)*

## CONCLUSIONS

The results indicate that construction materials can be manufactured with this alternative process, using industrial waste. These products will be aimed at wall cladding and, if they are to be used as flooring, their thickness will need to be increased. Even so, in both cases, the surface will need to be waterproofed to improve stain resistance, owing to the values obtained for open porosity.

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