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## **FEASIBILITY OF ALKALI-ACTIVATED MINING WASTE FOAMED MATERIALS INCORPORATING EXPANDED GRANULATED CORK**

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**Abstract:** Different combinations of mining waste mud, grounded waste glass, Portland cement, metakaolin and expanded cork were mixed together with alkaline activators (sodium silicate and sodium hydroxide solution) and as well aluminum powder or hydrogen peroxide to produce foamed lightweight materials. The size of the mineral materials is under 500  $\mu\text{m}$  and expanded cork particles size is between 2 to 4 mm. The expanded cork added to the mixes changed between 10 to 40% volume of total solids. The influence of expanded cork on compressive strength was investigated. Precursors and activators were mixed together to produce a homogeneous mixture, which was placed into a cubic mold (40 x 40 x 40  $\text{mm}^3$ ), and cured at a temperature of 60°C, for 24 hours. After curing process, samples without foaming agents achieved the maximum compressive strength of 14.7 and 19.5 MPa for 7 and 28 days respectively. The porosity was observed by the naked eye of large voids in range of 4 mm in size. Microstructure analyses were carried on by SEM. Samples made with aluminum powder showed higher volume increase about 358% compared with samples made with hydrogen peroxide that presented a 141% volume increase. This preliminary study shows the feasibility to produce new improved lightweight foamed alkali activated materials incorporating expanded cork with potential applications in artistic, architectural, and historical heritage restoration.

**Keywords:** *Alkali activated materials, mining waste mud, expanded cork, foamed materials, porosity*

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## INTRODUCTION

### INDUSTRIAL AND MINING WASTE GENERATION

Each year, a vast amount of industrial waste is generated from different sectors including mining, power and energy, and construction. In European countries, according to the most recent Eurostat data, about 29% of total waste generation in the EU-28 for 2012 (see Fig. 1), from economic activities and households is from mines and quarries (Eurostat et al. 2016). The significant amount of industrial wastes deposits has led to growing concerns about their ecological and environmental impacts, such the case of mining wastes (Castro-Gomes et al. 2012). Nowadays, for a circular and stronger green economy, a new ambitious circular economy package was adopted by the European Commission to help businesses and European Consumers to make the transition in which resources are used in a more sustainable way (European. Comission 2015). Furthermore, the public and the consumer prefer “green” products and processes, for that research and development activities are focused on the development of new products based industrial wastes, such is the case of mining wastes.

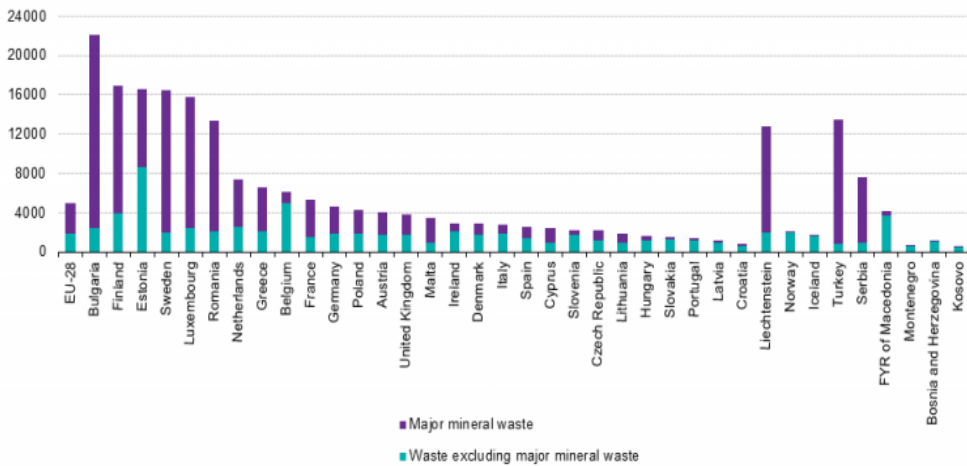


Fig. 1. Waste generation (including mineral waste), EU-28, 2012

### ALKALI ACTIVATED MATERIALS USING MINING WASTE

Research focused the attention on the reuse of waste materials (mining and quarrying) by integrating them into new materials manufacture such as typical applications include use in asphalt pavements (Castro-Gomes et al. 2002), in addition to other materials, as metakaolin (Strozi, Colombo, and Raymundo 2014), (J. L. Provis 2009), coal fly ash and waste glass (Zhu et al. 2016). The reuse of mineral wastes as precursor materials for alkali-activated binders is most promising by EU and other countries,

from an environmental, technical and economic point of view (Pacheco. Torgal 2008c), (Pacheco. Torgal 2009b)

First, these studies aimed for the development of new alkali-activated binder by reusing waste mud from a tungsten mining exploration (Panasqueira tungsten mine Fig. 2), that presents very good reactivity with alkaline activators and calcium hydroxide, for high alkali concentrations and curing at room temperature. Later, improved alkali-activation conditions were found out by mixing mining waste mud with different sources of silica (namely, river sand and amorphous ground waste glass) and cured at moderated temperatures, as presented in Tab. 1.



Fig. 2. Panasqueira mine, Covilhã, Portugal: Left: panoramic view of mine plant. Right: collection of mud from waste deposits

Tab. 1. Compressive strength (Rc) of alkali activated binders using Panasqueira mining waste mud

Author	Year	Mix Composition / (curing conditions)	Rc (MPa)	Ref
F. Pacheco-Torgal	2006	90% Mining waste mud <sup>c)</sup> + 10 % Calcium hydroxide Sodium hydroxide (16M) + Sodium silicate (28 days curing at room temperature)	30	(Pacheco-Torgal 2006)
F. Pacheco-Torgal	2008	90% Mining waste mud <sup>c)</sup> + 10 % Calcium hydroxide Sodium hydroxide (24M) + Sodium silicate (28 days curing at room temperature)	28	(Pacheco. Torgal 2008b)
F. Pacheco-Torgal	2009	90% Mining waste Mud <sup>c)</sup> + 10 % Calcium hydroxide Sodium hydroxide (24M) + Sodium silicate (28 days curing at room temperature)	28	(Pacheco-Torgal 2009a)
J. Centeio	2011	65% Mining waste Mud <sup>c)</sup> + 35% Sand Sodium hydroxide (10M) + Sodium silicate (3 days at 60°C curing temperature)	11	(J. Centeio 2011)
G. Kastiukas	2016	80 % Mining Waste Mud <sup>n)</sup> + 20 % Milled Glass Sodium hydroxide (10M) + Sodium silicate (24h at 60°C then curing at room temperature and testing at 28 days)	22	(Kastiukas, Zhou, and Castro-Gomes 2016)

<sup>c)</sup> – calcinated <sup>n)</sup> – non-calcinated

The alkaline activation of other aluminosiliceous industrial by-products is widely known to yield binders which make their properties comparable or even stronger and more durable than Conventional Portland Cement (Pacheco. Torgal 2009b), (L. Zhang, Ahmari, and Zhang 2011). As well, cost comparisons show this alkali activated cement repair solution is by far the most cost efficient (Pacheco. Torgal 2008a).

The opportunity to replace the Portland Cement (OPC) with those new alkali activated binders using mining waste was investigated by many researchers by enhanced environmental and durability performance (Pacheco. Torgal 2008a), (Longhi et al. 2016).

#### ALKALI ACTIVATED CEMENT HISTORY AND MAIN CONCEPTS

Since 1940, many researchers carried on studies to develop an alternative cementitious material to the conventional Portland Cement (Li, Sun, and Li 2010), (M.D. Roy 1999). Victor Glukhovsky prepare low-calcium and/or calcium-free cementitious materials by using clays and alkaline metal solution, calling “soil cement” for the resulting investigation about these alkali-activated materials in 1957 (Palomo et al. 2014). Tab. 1 presents a chronologically reviews some important events outlining steps in the development of alkali-activated cements.

A large variety of alkali-activated cements has been developed during the last of the two decades (Caijun. Shi et al. 2011), in accordance with different criteria such as technology, environment, economic and geographical rationality. Against this background of needed change and depending on the nature of (CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system), alkali-activated cements can be classified into three main categories (Palomo et al. 2014):

1. moderately calcium-rich cements.
2. low-calcium cements.
3. hybrid cements.

#### MECHANISM OF ALKALI-ACTIVATION: A CONCEPTUAL MODEL

The exact mechanism of alkali-activation, although deeply explored and investigated, is not yet completely defined: the employment of different kind of precursors and activators causes several changes in the chemistry of the reaction, affecting the quality and the characteristics of the final compounds. For this reason, it is possible to find several researches and documents in the literature, in which many authors tried to find out and explain which the different phases of alkali-activation are and what happens during them.

Tab. 2. Alkali-activated cement timeline (updated from (Palomo et al. 2014))

Author	Year	Significance	Ref.
Kühl	1930	Slag setting in the presence of dry potash	(Kühl. H 1930)
Feret	1939	Utilization of slag in cement	(R. Feret, 1939)
Purdon	1940	Alkali slag combination	(Purdon, A. 1940)
Glukhovsky	1959	Theoretical basis and development of alkaline cements	(V.D. Glukhovsky 1959)
P. R. Jochens	1969	Utilization of slags for the manufacture of cement	(Jochens 1969)
Davidovits	1981	Geopolymer chemistry and applications.	(Davidovits 2011)
Philip G. Malone	1985	Potential applications of Alkali Activated aluminosilicate binders in military.	(Malone 1985)
Davidovits	1987	Ancient and modern concretes compared.	(J Davidovits 1987)
Roy et al.	1989	Ancient concretes analogues.	(D.M. Roy et al. 1989)
Roy et al.	1990	Rapid setting alkali-activated cements.	(D.M. Roy et al. 1990)
Roy et al.	1992	Alkali-activated cements: an overview.	(D.M. Roy et al. 1992)
Palomo and Glasser	1992	CBC with metakaolin.	(A. Palomo et al. 1992)
Roy and Malek	1993	Slag cement.	(D.M. Roy et al. 1993)
Glukhovsky	1994	Ancient, modern, and future concretes.	(V.D. Glukhovsky 1994)
Wang and Scivener	1995	Slag and alkali-activated microstructure.	(Wang and Scivener 1995)
Palomo et al.	1999	Production of hardened cementitious materials from alkali-activated type F fly ashes	(Palomo, Grutzeck, and Blanco 1999)
Roy	1999	Opportunities and challenges of alkali-activated Cements.	(M.D. Roy 1999)
Shi	2006	First book on Alkali Activated cement.	(Shi 2006)
Duxson	2007	Geopolymer technology: the current state of the art2007.	(P. Duxon et al 2007)
Provis and Deventer	2009	Geopolymers: structure, processing, properties, and industrial applications.	(J. L. Provis 2009)
Rachit Ghosh et al.	2013	Fly Ash based-geopolymer -excellent short and long term properties-	(R. Ghosh et al. 2013)
Provis and Deventer	2014	Alkali-Activated Materials: State-of-the-Art Report	(J. L. Provis 2014)

(Purdon, A. 1940) was the first one who proposed a process of alkali-activation, mixing NaOH with variety of minerals and glass reach in silicon and/or aluminium including blast furnace slag. He discovered that the involved mechanism takes place in two steps:

- First: the release of silica, alumina, and lime.
- Second: formation of hydrated calcium silicates, aluminates as well as generation of alkali solution.

Following Purdon initial studies and based in current literature review (J. L. Provis 2009), Fig. 3, presents a scheme of general models for the alkali activation of aluminosiliceous materials.

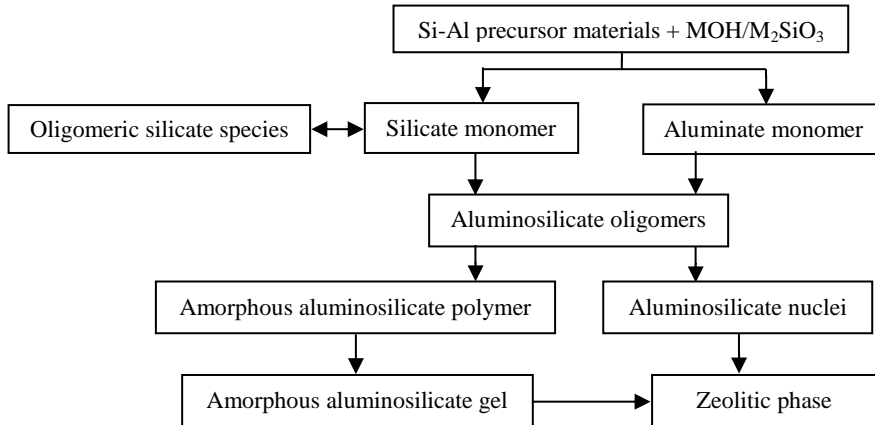


Fig. 3. Scheme for the mechanism of alkali activation, where M is a monovalent alkali cation, like sodium or potassium

#### ALKALI-ACTIVATED FOAMED MATERIALS

Recently, a novel idea has been suggested which involves the production of alkali-activated foamed materials. The idea combines the performance and benefits of energy savings obtained with lightweight foamed materials with the cradle-to-gate emissions reductions obtained by using a alkali-activated binder derived from an industrial by-product, like fly ash (Z. Zhang et al. 2014).

Pre-foaming and the mixed-foaming are two main methods having already been used to produce a foamed material (Narayanan and Ramamurthy 2000). A large kind of foaming agents have been produced for this purpose, as well as detergents, resin soap, glue resins, saponin, and hydrolyzed proteins, such as keratin and similar materials (Kearsley and Wainwright 2001).

Among of the methods used to produce lightweight alkali-activated foamed materials is the thermal expansion of (Na, K)-poly (sialate-multisiloxo) (Davidovits 2011) with ration Si:Al>>6. As well, to reduce the density of the foamed alkali-activated materials (Kovalchuk 2007), (Krivenko and Kovalchuk 2015), holes or lightweight aggregates (Aguilar, Díaz, and García 2010) can be added for such purpose.

In the last few years, several examples of alkali activated foams have been obtained from different raw and waste materials (Ehsan Ul Haq et al. 2015), (Feng et al. 2015). Tab. 3 reviews some important events outlining steps in the development of alkali-activated foamed materials in the last decade or so (also designated geopolymetric foamed materials). Various chemical foaming agents can be used in the foaming

process of inorganic polymers. Hydrogen-peroxide has been used to produce foams of inorganic polymers (Vaou and Panias 2010), (Strozi, Colombo, and Raymundo 2014), as well aluminium powder (Sanjayan et al. 2015), (P. Hlaváček et al. 2015), (Rickard and Riessen 2014) sodium-perborate (Abdollahnejad et al. 2015) as a chemical foaming agent. Accordingly, to Davidovits there is no standard formulation to fabricate an alkali-activated foam using hydrogen-peroxide. The successful of such foamed material requires a delicate optimization of two parameters (Davidovits 2011):

- (1) kinetics of peroxides decomposition with production of oxygen,
- (2) increase in viscosity of the geopolymer precondensate.

Tab. 3. Timeline of alkali-activated foamed materials.

Author	Year	Study/impact	Ref
Indrek Kulaots	2003	Possibility of standardizing the adsorption for use with coal fly ash pozzolans.	(Indrek K 2003)
Hwai-chung Wu	2007	Lightweight inorganic polymer	(Hwai-Chung Wu 2007)
V. Vaow et al.	2010	The ability of geopolymerization technology for production of thermal insulating foamy inorganic polymers	(Vaou and Panias 2010)
E. Prud'homme et al.	2011	The preparation of geopolymer foams based on potassium silicate, industrial waste, and various types of clays	(Prud et al. 2011)
M. Mustafa et al.	2012	The possibility of producing foam concrete by using a geopolymer system.	(Mustafa 2012)
S. Delair et al.	2012	The characterization of the behaviour of inorganic foams in aqueous media	(Delair et al. 2012)
Kun-Hsien Yang,	2013	The feasibility of using reservoir sludge as a raw material in the production of foamed inorganic polymers with different densities.	(Yang. k et al. 2013)
Marcelo Strozi-Cilla	2014	Geopolymer foams by gelcasting	(Strozi, Colombo, and Raymundo 2014)
G. Masi et al.	2014	Foaming to reduce the density of geopolymeric materials	(Masi et al. 2014)
Z. Abdollahnejad	2015	Properties of foam geopolymers.	(Abdollahnejad et al. 2015)
P. Hlavacek et al.	2015	Synthesis of inorganic fly ash-based foam	(P. Hlaváček et al. 2015)
Z. Abdollahnejad	2016	Development of Foam One-Part Geopolymers	(Z.abdollahnejade 2016)
V. Ducman	2016	Characterization of geopolymer fly ash based foams obtained with the addition of Al powder or H <sub>2</sub> O <sub>2</sub> as foaming agents	(M. Rebeiro et al. 2004)

Besides, the reaction between the aluminum metal powder and alkaline activator also takes place rapidly and releases hydrogen (Aguilar, Díaz, and García 2010), (Sanjayan et al. 2015). The releasing of hydrogen gas result from a very rapid reaction (equation (1)) (P. Hlaváček et al. 2015).



The hydrogen-peroxide ( $\text{H}_2\text{O}_2$ ) is thermodynamically unstable and therefore can be easily decomposed to water and oxygen gas (equation (2)) with the latter playing the role of the geopolymeric paste blowing agent (Vaou and Panias 2010):



#### ALAKLI-ACTIVATED MATERIALS WITH LIGHTWEIGHTAGGREGATES

Besides foaming, density reduction (Marcos and Alves 2014) of alkali-activated materials can be done by using lightweight aggregate, as alternative to the normal weight granules, where they show better thermal insulating features.

Alkali-activated materials with lightweight aggregates for non-structural applications are usually produced with artificial aggregates such as expanded clay, expanded polystyrene (EPS) or granulated cork (Marcos and Alves 2014).

The use of granulated cork has been studied in various industries as lightweight aggregate. (F. Branco et al. 2006) have developed a research project assessing physical and mechanical properties of waste cork, and exploring its potential benefits when using as aggregates in concrete production (Matos, Nunes, and Sousa-coutinho 2015).

Cork granules are a by-product (Karade, Irle, and Maher 2006) from the industry and the fact that cork is a natural product their usage has eco-efficient advantages (A. Brás et al. 2013). Cork granules are of low density and could be used as lightweight aggregate for manufacturing concrete and mortars (namely polymer modified mortars) with superior thermal and acoustic insulation properties and higher deformability (A. Brás et al. 2013), as well with high durability, very low permeability, and high resistance to chemical and frost attack (M. Ribeiro et al. 2004).

Nowadays, cork is used in a wide range of application in the building as a solution of lightweight, thermal insulating and shows good environmental advantages (Matos, Nunes, and Sousa-coutinho 2015). (Panesar and Shindman 2012) studied the impact of cork used as an alternative of sand or an alternative of stone on the plastic, mechanical, transport, microstructural and thermal properties of mortar and concrete. (Karade, Irle, and Maher 2006) studied the influence of cork granules for the manufacture compatibility with cement and the hydration test results showed that cork granules (both natural and expanded) are compatible with cement and can be added up to 30% by weight of cement.



## PRODUCTION OF EXPANDED GRANULATED CORK

Cork is the bark of the cork oak (*Quercus suber* L). Before using it in several applications the cork bark it is left to dry in the sun and is then boiled to soften it. The best bits of cork are punched out to make bottle corks. The remainder of the cork is used in many applications, namely in buildings as agglomerated cork products (2016, January 18) Retrieved from <http://www.corklink.com/index.php/about-cork/>. In Portugal, there are more than 720 thousand hectares of cork forests. Besides, cork oak grows in Mediterranean regions such as Spain, Italy, France, Morocco, and Algeria (Gil 1998). For most applications; cork must be boiled first to make it more pliable then to fully expand the lenticels. Initially, after boiling (for about 1 hour), the cork cells will be collapsed and wrinkled, the interior gas in the cells expands to create a very tight, uniform cell structure (Helena Pereira 1987). Expanded cork is made from the bark of cork tree. Because the cork used to make expanded cork is of lower quality (usually contains a high percentage of wood) it is grounded down to 20mm size granules and then it is steam heated up to 400°C for about 2 hours. The expanded cork used in this work was provided by (SOFALCA Sociedade Central de Produtos de Cortiça, Lda, Abrantes, Portugal). The cell structure of the expanded cork is presented in Fig. 4.

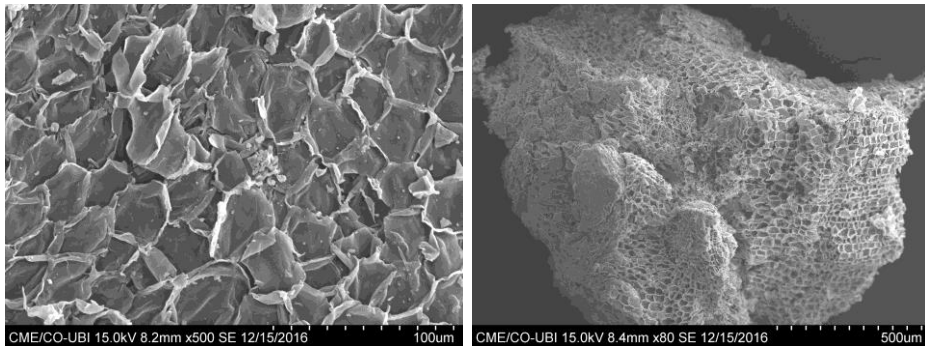


Fig. 4. Expanded cork granules at high and low magnification (SEM micrographs obtain at UBI optical center)

## MATERIALS, METHODS, AND RESULTS

Alkali-activated materials and expanded granulated cork were combined, together, for the feasibility of developing lightweight alkali-activated materials (LWAAM). As described in the next section properties such as density, compressive strength, porosity, were determined in LWAAM containing different percentages of expanded cork particles, and microstructure characterization was carried on by SEM.

## MATERIALS AND LWAAM MIX DESIGN

Tungsten mining waste mud (WM) obtained from the Panasqueira mine was used as aluminosilicate rich precursor.

Tab. 4. Oxide chemical composition and Blaine specific surface of precursors

Oxide / Materials	Constituents (%)								Blaine fineness (cm <sup>2</sup> /g)
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	CaO	SO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	
Waste mud	46.67	17.01	4.90	0.85	0.69	7.90	15.47	4.83	742
Milled Glass	68.13	2.80	0.86	12.52	10.52	0.23	2.90	2.04	2665
Metakaolin	52.28	42.99	0.94	0.32	-	-	1.49	0.47	4467
Cement	10.02	2.62	1.83	0.09	76.79	5.03	2.49	1.05	4006

Cement – SECIL CEM II/B-L 35.2N; Metakaolin –(BASF- the chemical company)

A percentage of 10 wt.% of the WM was replaced with milled glass powder (MG), other 5 wt.% was replaced by metakaolin, and another 5 wt.% was replaced by Portland cement (OPC), in several combinations. MG and metakaolin were added to the WM to increase alkali-activation reactivity, particularly by adding more quantity of amorphous SiO<sub>2</sub> since WM is composed mainly by muscovite and quartz with very low reactivity even after calcination (Pacheco. Torgal 2008c). In this study, WM was not calcinated. OPC was added to accelerate the curing time (Nath and Sarker 2015).

Tab 5. Chemical composition of activators

Oxide / Materials	Chemical composition of activator (g)					
	Na <sub>2</sub> O	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	K <sub>2</sub> O	CaO
SS- Sodium silicate	19.37	62.60	0.90	142.32	-	-
SH- Sodium hydroxide	13.02	0.000	0.000	43.27	-	-

Typical chemical composition of precursors is presented in Tab 4. Composition was determined, in several samples of WM, MG, metakaolin and OPC, by energy dispersive spectrometry (SEM/EDS). In case of WM it consists mainly of silica and alumina with smaller percentage of iron and potassium. Tab. 5 presents the chemical composition of precursors as given by suppliers (José Manuel Gomes dos Santos, Lda., LUXCITANIA, Lda). SEM images of the WM, MG, metakaolin, and OPC are given in Fig. 5.

Tab 6. Mix design formulation

	WM - Waste Mud (g)	MG - Milled Glass (g)	OPC- Cement (g)	Metakaolin (g)	EG Cork (g) (%)	Activators (g)		HP - Hydrogen Peroxide (g)	AL - aluminium powder (g)	P/A Ratio	SS/SH Ratio
						SS	SH				
CP	739.09	75.50	44.62	39.25	0	205.36	51.34	0	0	3.5	4
LW1	665.18	67.95	40.16	35.33	4.03 (10%)	184.82	46.21	0	0	3.5	4
	591.27	60.40	35.70	31.40	8.06 (20%)	164.29	41.07	0	0	3.5	4
	517.36	52.85	31.23	27.48	12.10 (30%)	143.75	35.94	0	0	3.5	4
	443.46	45.30	26.77	23.55	16.13 (40%)	123.21	30.80	0	0	3.5	4
LW2	105.58	10.79	12.75	0	20%	36.89	9.22	1.29	0	2.8	4
	105.58	10.79	12.75	0	20%	36.89	9.22	2.58	0	2.8	4
	105.58	10.79	12.75	0	20%	36.89	9.22	3.87	0	2.8	4
LW3	105.58	10.79	12.75	0	20%	29.79	19.86	0	1.29	2.6	1.5
	105.58	10.79	12.75	0	20%	29.79	19.86	0	2.58	2.6	1.5
	105.58	10.79	12.75	0	20%	29.79	19.86	0	3.87	2.6	1.5

(%) – Percentage of precursors total volume; P- precursors; A- activators

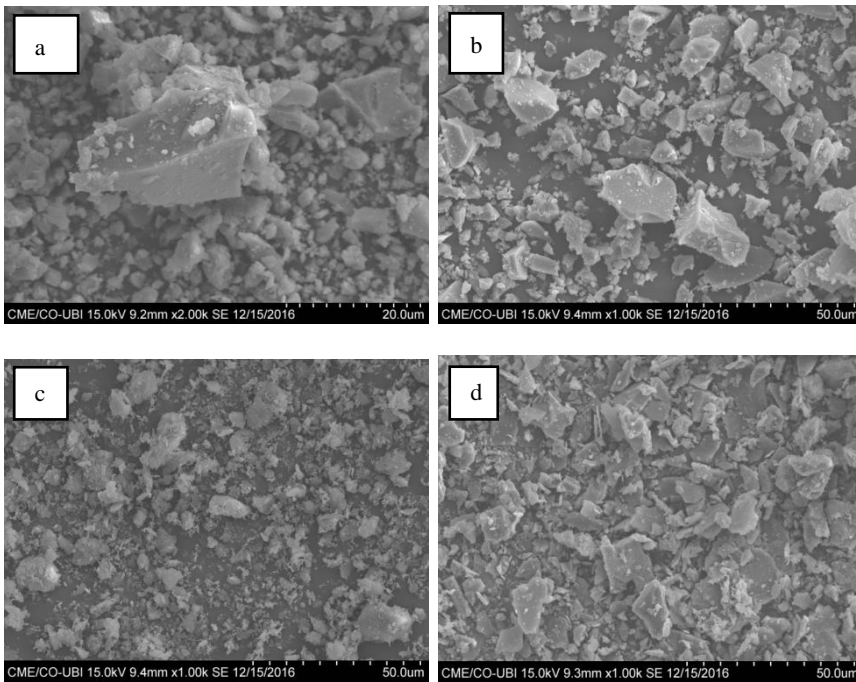


Fig. 5. SEM micrographs high magnification: (a) OPC CEM II/B-L 35.2N (2000x), (b) MG-milled glass (1000x), (c) Metakaolin (1000x), and (d) WM-mining waste mud (1000x)

## METHODS AND TESTING

The WM-waste mud powder, MG-milled waste glass, OPC-Portland cement, metakaolin and (EG cork) expanded granulate cork were firstly mixed in a dry state for 1 min. The activators (10M SH-sodium hydroxide + SS-sodium silicate) were mixed using a magnetic stirrer for 5 min at 500 RPM. The dry mixture and activators solution were combined in a bench top mixer and mixed using an average speed for 2 min and another 1 min at high speed to produce (CP) and (LW1). For the (LW2) the Al powder was added first with the dry mixture whereas for the (LW3) HP-hydrogen peroxide was added in the wet mixture after full mixing with activators solution and mixed by hand. The process to produce foamed material by using an alkali-activation system is explained in the diagrams of Fig. 6.

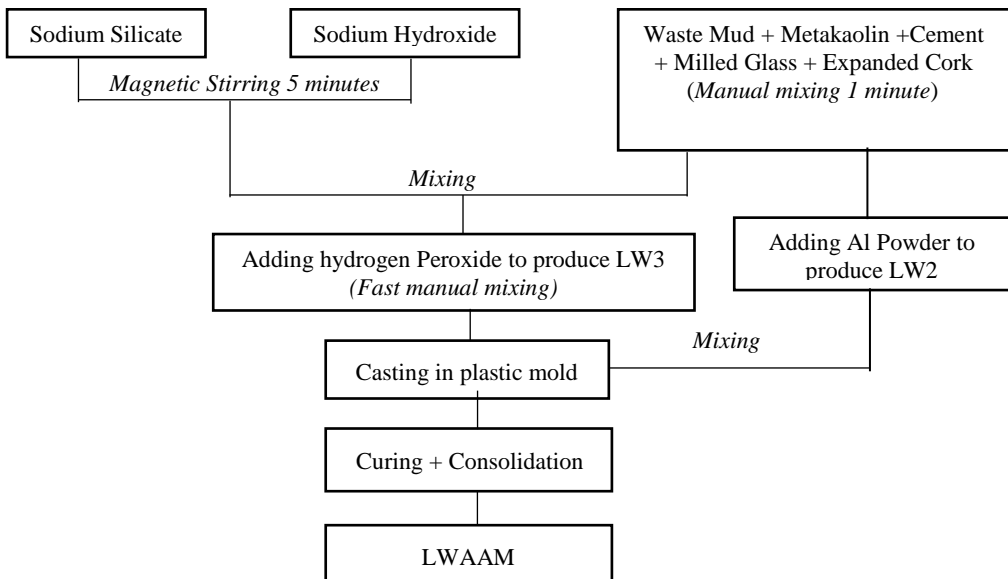


Fig. 6. Schematic process for the formation of lightweight alkali-activated foamed material.

The mixes were poured into  $40 \times 40 \times 40 \text{ mm}^3$  moulds. The mixes were placed in the oven at  $60 \text{ }^\circ\text{C}$  for 24 h to speed up the alkali-activation. After curing in the oven, the samples were demoulded and left to cure in ambient laboratory conditions until testing of the compressive strength at 7 and 28 days. The compressive strength test for the LW1 was made with (ADR Touch ELE international limited machine, at the construction technology and mechanic test laboratory, DECA-UBI). Whereas, LW2 and LW3 was tested with (AUTOGRAPH AGS-X, 10KN SHIMADZU machine in the mechanics of materials and mechanical technology laboratory, DECA-UBI).

The porosity of each cube sample was measured accordingly to the EN 12390 – 7: 2009 Standard with some modifications. One specimen from each batch were oven-dried at  $60 \text{ }^\circ\text{C} \pm 5 \text{ }^\circ\text{C}$  for 24 h to achieve a constant weight before testing. Porosity was calculated for LW1 mixes using Eq. (3):

$$\text{Porosity (\%)} = (W_s - W_d) / W_d \times 100 \quad (3)$$

where  $W_s$  is the saturated weight (g) and  $W_d$  is the oven-dry weight (g).

Before testing, the LW1 specimens were weighed to determine their density. The compressive strength of the specimens was performed on cubic samples ( $40 \text{ mm} \times 40 \text{ mm} \times 40 \text{ mm}$ ) after curing process at the ages of 7 and 28 days. The average values from the three specimens was calculated.

## RESULTS AND DISCUSSION

### DENSITY, POROSITY, AND VOLUME EXPANSION

The density and porosity of LW1 incorporating expanded granulated cork is shown in Fig. 7. Density reduces for increasing expanded cork particles content (from about 2000 to  $1670 \text{ kg/m}^3$ ). The lowest density was found in the mixture with 40 vol.% expanded cork. In general, an increase in cork particles content led to lower density, as expected.

The percentage of porosity of LW1 mix without cork is about 11,5%, increasing up to 14% for 40 vol.% of expanded cork content.

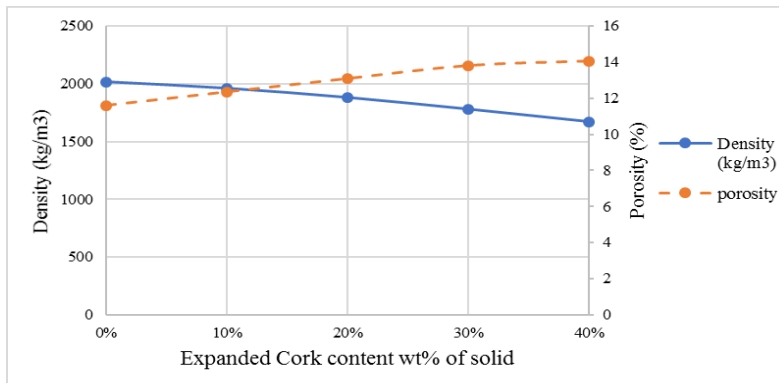


Fig. 7. Change of density and porosity for LW1 as a function of expanded cork particles content; ( $60^\circ\text{C}$  24h)

Figures 9 and 10 show typical volume expansion in LW2 and LW3 mixes using hydrogen peroxide (HP) and aluminum powder (AL), respectively. For LW3 the volume expansion increases changes by 150 %, 250% and 358% with 1%, 2% and 3% aluminum powder content. While, for LW2 the volume expansion increases changes by about 84%, 137% and 141% with 1%, 2% and 3% hydrogen peroxide content. Because of the fast reaction between the hydrogen peroxide and the aqueous solution in the mix, it decomposes very quickly and produces oxygen gas. It was observed in the mixes LW2 that the expansion time is very small. The same case when the aluminum powder find the NaOH as a good catalyzer since we decrease the SS/SH ratio to 2.6. the releasing of hydrogen gas was very quickly and the expansion time very short.

### COMPRESSIVE STRENGTH

In this preliminary study, we also determined LW1 compressive strength for different expanded granulated cork content. The results presented in Fig. 9 show the compressive strength increases from 14.7 MPa at 7 days to 19.5 MPa at 28 days for zero expanded cork incorporation. For 20 vol.% incorporation compressive strength is about 14 MPa at 28 days while for 40% volume incorporation it decreases up to 11 MPa.

However, for LW2 and LW3 foamed mixes incorporating 20% volume of expanded cork we found out porosity strongly affects the compressive strength, since all mixes presented a compressive strength lower than 1 MPa. It was also found out by other authors (P. Hlaváček et al. 2015), (Abdollahnejad et al. 2015) that porosity and the pore size distribution greatly influenced the properties of the LWAAM though alkali-activated foamed materials can be produced with a relatively high compressive strength as is aimed in future research work.

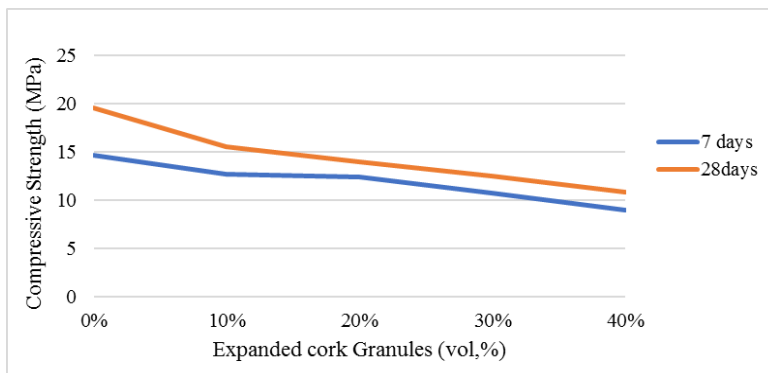
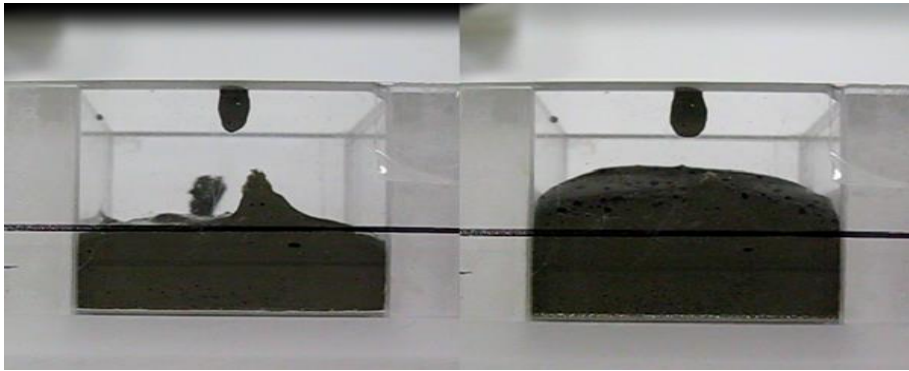
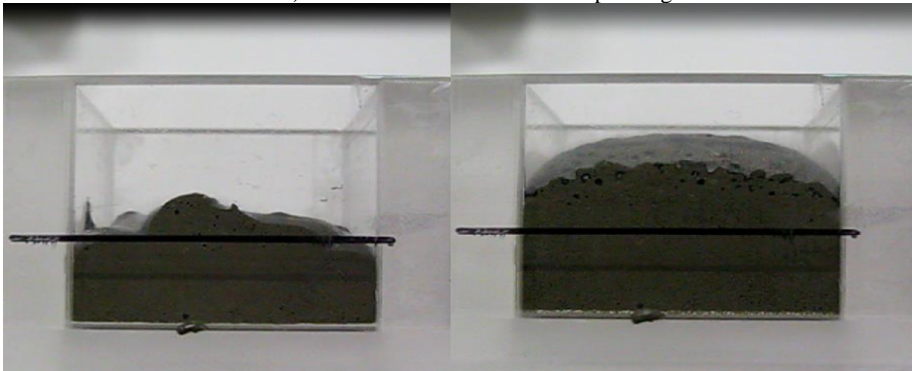


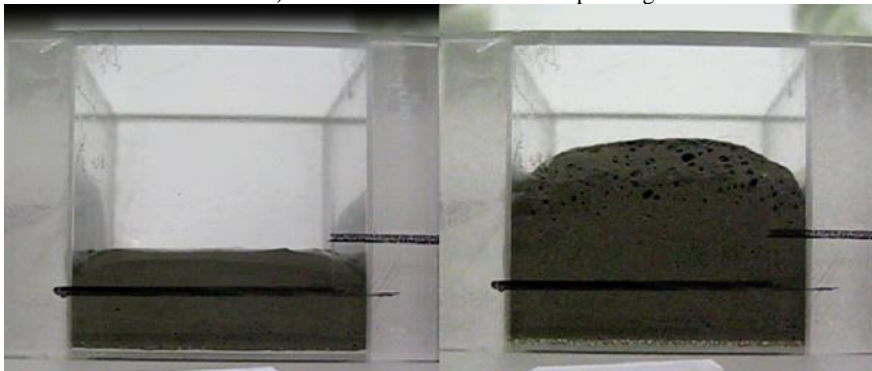
Fig. 8. Compressive strength for LW1 with different (vol.%) of expanded cork particle



a) 1% HP. Before and after expanding.



b) 2% HP. Before and after expanding.



c) 3% HP. Before and after expanding.

Fig. 9. Volume expansion using hydrogen peroxide (HP)

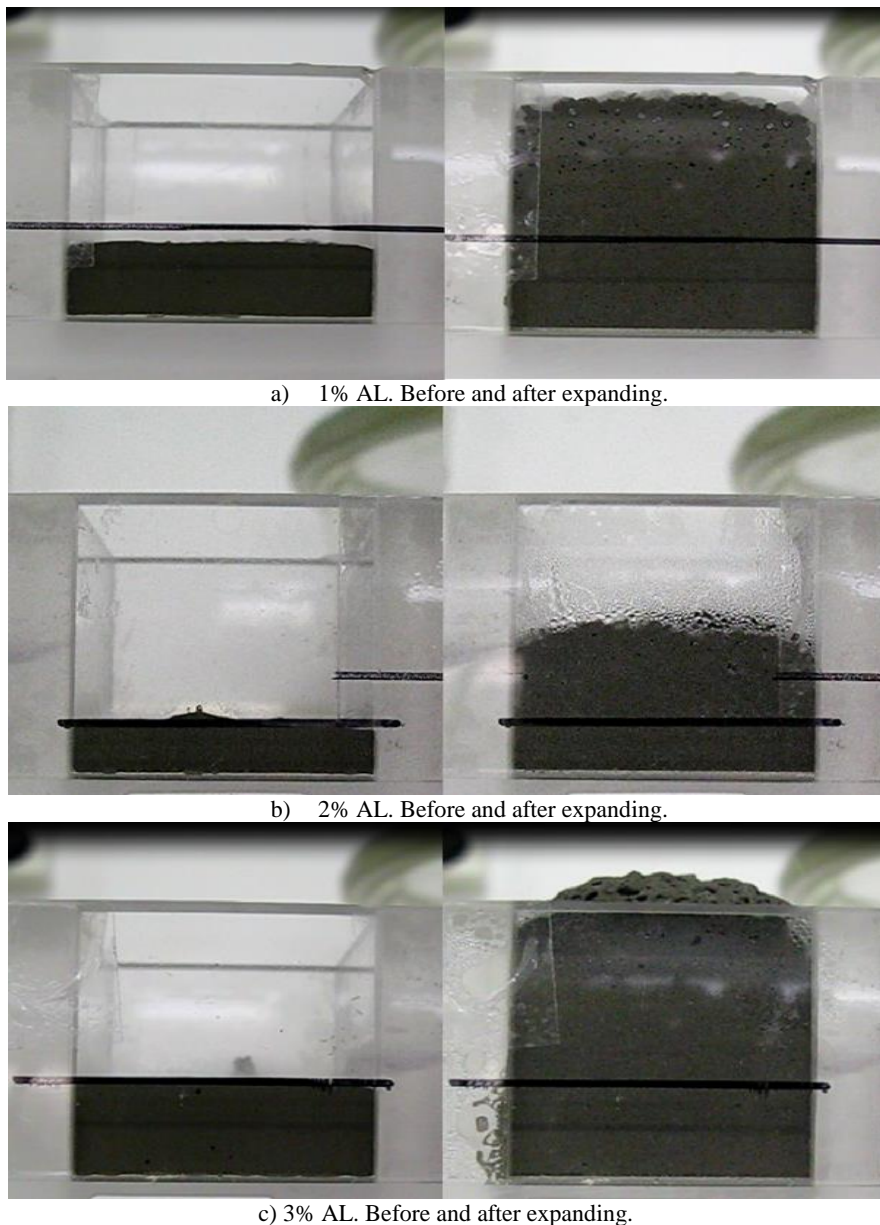


Fig. 10. Volume expansion using aluminium Powder (AL)

The expansion time was very fast and the reaction between the hydrogen peroxide (HP) and the catalyser start immediately when we added it to the mix LW2, while that the LW3 is about 3 minutes from the reaction start to the end of the expansion.



## MICROSTRUCTURAL STUDIES

SEM analysis for distribution and size of pores is presented in Fig. 11. The microstructure of the foams was examined by high resolution images in the Scanning Electron Microscope (HITACHI S-3400N) micrographs at the UBI optical center. The pore size for foamed samples LW2 and LW3 are ranged between 42.3  $\mu\text{m}$  small diameter pores to 4 mm diameter large voids, and the distributions of the pores in both samples were found out to be relatively uniform. Accordingly, to other authors, the pores are normally closed and almost spherical when the content of  $\text{H}_2\text{O}_2$  in the paste is low. If the content of  $\text{H}_2\text{O}_2$  increase coalescence occurs among cells and the cells' geometrical shape change from spherical to oval (Vaou and Panias 2010). This features were also found out in this research work.

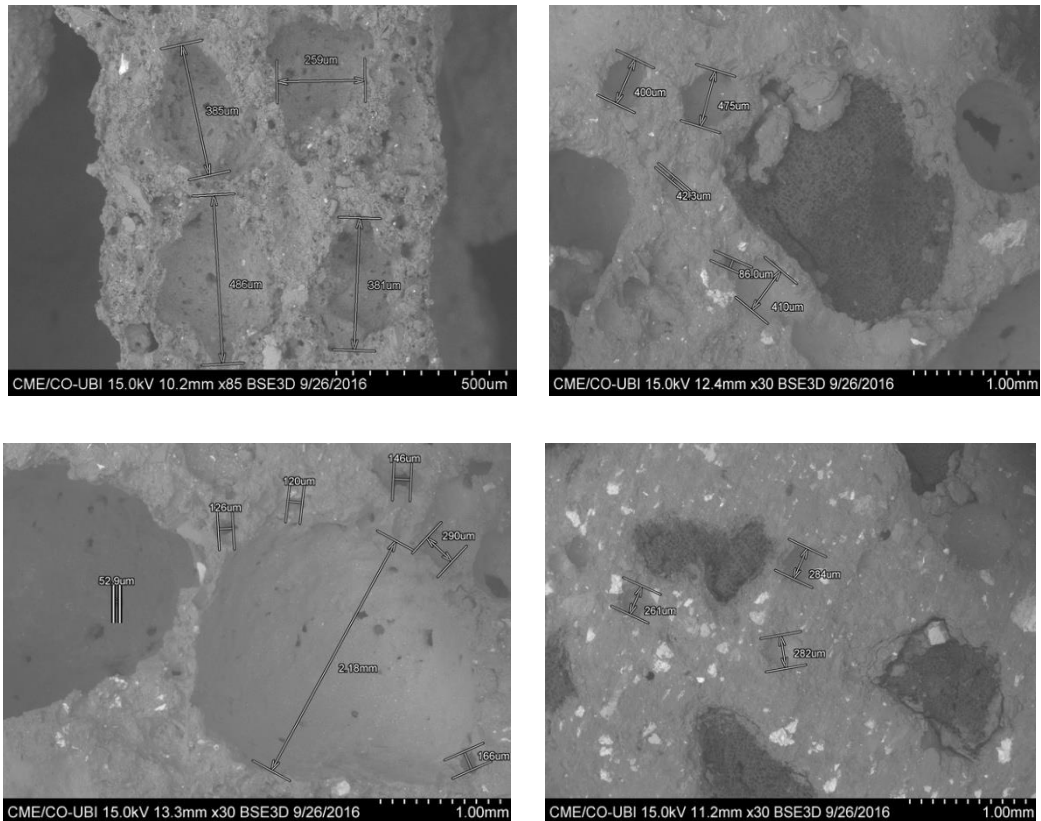


Fig. 11. SEM analysis for distribution and size of pores. Left: LW2 (2% hydrogen peroxide); Right: LW3 (2% aluminium powder)

## CONCLUSIONS

This paper describes a preliminary study of making light weight alkali-activated materials (LWAAM) using Panasqueira waste mud incorporating expanded granulated cork. A series of mixes were prepared, containing mining waste mud, milled waste glass, metakaolin and Ordinary Portland Cement, in different proportions. The influence on porosity, density, and compressive strength of incorporating granulated expanded cork at different percentages was studied first. The volume expansion obtained by Al-aluminium powder and HP-hydrogen peroxide, as foaming agents, for a mix containing 20% of expanded cork, was also carried on. From the whole study the following main conclusions can be obtained:

- Density of LWAAM decreases with an increase in expanded granulated cork particle content, while porosity increases, as expected;
- A density of about  $1650 \text{ kg/m}^3$  was obtained for foamed LWAAM with 40% volume of incorporated expanded granulated cork particles;
- A compressive strength of 14 MPa was obtained for 20% volume content of expanded cork for light weight alkali-activated material (LWAAM);
- The compressive strength of foamed LWAAM incorporating 20% volume of expanded cork is very low, of about 1 MPa;
- Volume expansion of foamed LWAAM increases by 150%, 250% and 358% for 1%, 2% and 3% aluminum powder, respectively, as foamed agent;
- While, the volume expansion of foamed LWAAM changes by about 84%, 137% and 141% for 1%, 2% and 3% hydrogen peroxide content;

The pore size of foamed LWAAM varies between  $42.3 \mu\text{m}$  small diameter pores to 4 mm diameter large voids;

Aluminum powder foaming agent gives a higher volume increase of about 360% when compared with hydrogen peroxide that give a lower volume increase of about 140%;

According to this preliminary study, it is feasible to produce foamed light weight alkali-activated materials (foamed LWAAM) using Panasqueira waste mud and other precursor materials, as well incorporating expanded granulated cork. Foamed LWAAM can be used in several applications where low density and fire resistance is required. However, from the obtained results it can also be concluded that the compressive strength of foamed LWAAM is very low (about 1MPa) which is a critical aspect that needs research for future improvement.

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#### REFERENCES

- A. Brás et al. 2013. “Cement-Cork Mortars for Thermal Bridges Correction . Comparison with Cement- EPS Mortars Performance” 49: 315–27. doi:10.1016/j.conbuildmat.2013.08.006.
- Abdollahnejad, Z, F Pacheco-torgal, T Félix, W Tahri, and J Barroso Aguiar. 2015. “Mix Design , Properties and Cost Analysis of Fly Ash-Based Geopolymer Foam.” *Construction and Building Materials* 80 (May 2010). Elsevier Ltd: 18–30. doi:10.1016/j.conbuildmat.2015.01.063.
- Aguilar, R Arellano, O Burciaga Díaz, and J I Escalante García. 2010. “Lightweight Concretes of Activated Metakaolin-Fly Ash Binders , with Blast Furnace Slag Aggregates.” *Construction and Building Materials* 24 (7). Elsevier Ltd: 1166–75. doi:10.1016/j.conbuildmat.2009.12.024.
- Caijun. Shi et al. 2011. “New Cements for the 21st Century : The Pursuit of an Alternative to Portland Cement”. *Cement and Concrete Research* 41 (7). Elsevier B.V.: 750–63. doi:10.1016/j.cemconres.2011.03.016.
- Castro-gomes, J P, Abílio P Silva, Rafael P Cano, J Durán Suarez, and A Albuquerque. 2012. “Potential for Reuse of Tungsten Mining Waste-Rock in Technical-Artistic Value Added Products.” *Journal of Cleaner Production* 25. Elsevier Ltd: 34–41. doi:10.1016/j.jclepro.2011.11.064.
- Castro Gomes et al. 2002. “Valorizacao\_de\_residuos\_de\_minas\_em\_pavi.pdf.”
- Davidovits, J. 2011. *Geopolymer Chemistry and Applications 3rd Edition*.
- Delair, Stéphanie, Élodie Prud, Claire Peyratout, Agnès Smith, Philippe Michaud, Lilian Eloy, Emmanuel Joussein, and Sylvie Rossignol. 2012. “Durability of Inorganic Foam in Solution : The Role of Alkali Elements in the Geopolymer Network” 59: 213–21. doi:10.1016/j.corsci.2012.03.002.
- Ehsan Ul Haq et al. 2015. “Microwave Synthesis of Thermal Insulating Foams from Coal Derived Bottom Ash,” no. February. doi:10.1016/j.fuproc.2014.10.017.
- European. Commission. 2015. “European Commission, Press Release - Closing the Loop: Commission Adopts Ambitious New Circular Economy Package to Boost Competitiveness, Create Jobs and Generate Sustainable Growth.” *Press Release*, no. December.
- Eurostat, Further, European Union, European Parliament, E C Article, Further Eurostat, Member States, E U Member States, E U Member States, and Member States. 2016. “Waste Statistics Main Statistical Findings Total Waste Generation” 2012 (September 2015).
- F. Branco et al. 2006. “Utilização Da Cortiça Como Agregado Em Betões.pdf.”
- Feng, Junjie, Ruifang Zhang, Lunlun Gong, Ye Li, Wei Cao, and Xudong Cheng. 2015. “Development of Porous Fly Ash-Based Geopolymer with Low Thermal Conductivity” 65: 529–33. doi:10.1016/j.matdes.2014.09.024.
- Gil, Luis. 1998. Cortiça: produção, tecnologia e aplicação, in: “Cork : Properties , Capabilities and Applications” 50 (6): 345–65. doi:10.1179/174328005X41168.

- Helena Pereira. 1987. "The Cellular Structure of Cork from Quercus," no. January. doi:10.1163/22941932-90001048.
- Hwai-Chung Wu. 2007. "New Building Materials from Fly Ash-Based Lightweight Inorganic Polymer" 21: 211–17. doi:10.1016/j.conbuildmat.2005.06.052.
- Indrek K. 2003. "Adsorption of Surfactants on Unburned Carbon in Fly Ash and Development of a Standardized Foam Index Test" 33: 2091–99. doi:10.1016/S0008-8846(03)00232-1.
- J. Davidovits, Ancient and modern concretes: what is the real difference, *Concrete International*, December (1987) 23–38. in: D.M. Roy, Alkali-activated cements Opportunities and challenges, 29 (1999) 249–254.
- J. Centeio. 2011. "Propriedades Físicas de Argamassa Geopolimérica de Lamas Residuais Das Minas Da Panasqueira."
- J. L. Provis. 2009. *Geopolymers - Structure, Processing, Properties and Industrial Applications Jhon L. Provis.pdf*.
- J. L. Provis. 2014. *Alkali Activated Materials State of the Art Report*.
- Jochens, P. R. 1969. "Utilization of slags for the manufacture of cement", *Journal of the South African Institute of Mining and Metallurgy*, 464–74.
- Karade, Sukhdeo R, Mark Irle, and Kevin Maher. 2006. "Influence of Granule Properties and Concentration on Cork-Cement Compatibility," 281–86. doi:10.1007/s00107-006-0103-2.
- Kastiukas, Gediminas, Xiangming Zhou, and João Castro-gomes. 2016. "Development and Optimisation of Phase Change Material-Impregnated Lightweight Aggregates for Geopolymer Composites Made from Aluminosilicate Rich Mud and Milled Glass Powder." *Construction and Building Materials* 110. Elsevier Ltd: 201–10. doi:10.1016/j.conbuildmat.2016.02.029.
- Kearsley, E P, and P J Wainwright. 2001. "The Effect of High Fly Ash Content on the Compressive Strength of Foamed Concrete" 31: 0–7.
- Kovalchuk, P V Krivenko Æ G Yu. 2007. "Directed Synthesis of Alkaline Aluminosilicate Minerals in a Geocement Matrix," 2944–52. doi:10.1007/s10853-006-0528-3.
- Krivenko, Pavel, and Georgiy Kovalchuk. 2015. "Achieving a Heat Resistance of Cellular Concrete Based on Alkali Activated Fly Ash Cements," 599–606. doi:10.1617/s11527-014-0479-0.
- Kühl, H. (1930) *Zementchemie*. Berlin, Germany. Verlag Technik, Band III; 1958 or Zement 19, in: A. Palomo, P. Krivenko, E. Kavalerova, O. Maltseva, A review on alkaline activation : new analytical perspectives, 64 (2014).
- Li, Chao, Henghu Sun, and Longtu Li. 2010. "Cement and Concrete Research A Review: The Comparison between Alkali-Activated Slag ( Si + Ca ) and Metakaolin ( Si + Al ) Cements." *Cement and Concrete Research* 40 (9). Elsevier Ltd: 1341–49. doi:10.1016/j.cemconres.2010.03.020.
- Longhi, A, Erich D Rodríguez, Susan A Bernal, John L Provis, and Ana Paula. 2016. "Valorisation of a Kaolin Mining Waste for the Production of Geopolymers" 115. doi:10.1016/j.jclepro.2015.12.011.
- M. Rebeiro et al. 2004. "Characterization of Lightweight Polymer Mortar Modified with Cork Granulates" 64: 2197–2205. doi:10.1016/j.compscitech.2004.03.006.
- M.D. Roy. 1999. "Alkali-Activated Cements Opportunities and Challenges" 29: 249–54.
- Malone, Philip G et al. 1985. "Potential applications of alkali activated alumino-silicate binders in military operations"
- M. D. Roy, C.A. Langton, Studies of Ancient Concrete as Analogues of Cementitious Sealing Materials for a Repository in Tuff, LA- 11527-MS, Los Alamos National Laboratory, Los Alamos, NM, March 1989. in: D.M. Roy, Alkali-activated cements Opportunities and challenges, 29 (1999) 249–254.
- M. D. Roy, et al. 1990 Wolfe-Confer, New rapid setting alkali activated cement compositions, MRS Proceedings, 179 (1990) 203–220. in: D.M. Roy, Alkali-activated cements Opportunities and challenges, 29 (1999) 249–254.

- M. D. Roy, M.R. Silsbee, Alkali-activated materials: an overview, MRS Proceedings, 245 (1992) 153–164. in: D.M. Roy, Alkali-activated cements Opportunities and challenges, 29 (1999) 249–254.
- M. D. Roy, R.I.A. Malek, Hydration of slag cement, progress in cement and concrete science and technology, in: S.N. Ghosh, S.L. Sarkar, S. Harsh (Eds.), Mineral Admixtures in Cement and Concrete, Volume. in: D.M. Roy, Alkali-activated cements Opportunities and challenges, 29 (1999) 249–254. 4, ABI Books Pvt. Ltd., New Delhi, India, 1993, pp. 84–117.
- Marcos, Diogo, and Paiva Alves. 2014. “Non - Structural Lightweight Concrete Produced with Volcanic Scoria from São Miguel Island,” 1–12.
- Masi, Giulia, William D A Rickard, Les Vickers, Maria Chiara, and Arie Van Riessen. 2014. “A Comparison between Different Foaming Methods for the Synthesis of Light Weight Geopolymers.” *Ceramics International* 40 (9). Elsevier: 13891–902. doi:10.1016/j.ceramint.2014.05.108.
- Matos, Ana Mafalda, Sandra Nunes, and Joana Sousa-coutinho. 2015. “Cork Waste in Cement Based Materials.” *JMADE* 85. Elsevier B.V.: 230–39. doi:10.1016/j.matdes.2015.06.082.
- Mustafa, Bakri. 2012. “Fly Ash-Based Geopolymer Lightweight Concrete Using Foaming Agent,” 7186–98. doi:10.3390/ijms13067186.
- Narayanan, N, and K Ramamurthy. 2000. “Structure and Properties of Aerated Concrete : A Review” 22: 321–29.
- Nath, Pradip, and Prabir Kumar Sarker. 2015. “Use of OPC to Improve Setting and Early Strength Properties of Low Calcium Fly Ash Geopolymer Concrete Cured at Room Temperature.” *CEMENT AND CONCRETE COMPOSITES* 55. Elsevier Ltd: 205–14. doi:10.1016/j.cemconcomp.2014.08.008.
- P. Duxon et al. 2007. “Geopolymer Technology : The Current State of the Art,” no. 4: 2917–33. doi:10.1007/s10853-006-0637-z.
- P. Hlaváček et al. 2015. “Inorganic Foams Made from Alkali-Activated Fly Ash : Mechanical , Chemical and Physical Properties” 35: 703–9. doi:10.1016/j.jeurceramsoc.2014.08.024.
- Pacheco, Torgal. 2006. “Desenvolvimento de ligantes obtidos por activação alcalina de lamas residuais das minas da Panasqueira.”, Tese de Doutoramento, Universidade da Beira Interior. Portugal.
- Pacheco, Torgal. 2008a. “Adhesion Characterization of Tungsten Mine Waste Geopolymeric Binder . Influence of OPC Concrete Substrate Surface Treatment” 22: 154–61. doi:10.1016/j.conbuildmat.2006.10.005.
- Pacheco, Torgal. 2008b. “Investigations of Tungsten Mine Waste Geopolymeric Binder : Strength and Microstructure” 22: 2212–19. doi:10.1016/j.conbuildmat.2007.08.003.
- Pacheco, Torgal. 2008c. “Properties of Tungsten Mine Waste Geopolymeric Binder” 22: 1201–11. doi:10.1016/j.conbuildmat.2007.01.022.
- Pacheco, Torgal. 2009a. “Tungsten Mine Waste Geopolymeric Binder : Preliminary Hydration Products Investigations” 23: 200–209. doi:10.1016/j.conbuildmat.2008.01.003.
- Pacheco, Torgal. 2009b. “Utilization of Mining Wastes to Produce Geopolymeric Binders.” In , 267–91.
- Palomo, A, M W Grutzeck, and M T Blanco. 1999. “Alkali-Activated Fly Ashes A Cement for the Future” 29: 1323–29.
- Palomo, A, P Krivenko, E Kavalerova, and O Maltseva. 2014. “A Review on Alkaline Activation : New Analytical Perspectives” 64 (31).
- Palomo, A. F.P. Glasser, British Ceramic Transactions and Journal 91, (1992) 107–112. in: D.M. Roy, Alkali-activated cements Opportunities and challenges, 29 (1999) 249–254.
- Panesar, D K, and B Shindman. 2012. “The Mechanical , Transport and Thermal Properties of Mortar and Concrete Containing Waste Cork.” *Cement and Concrete Composites* 34 (9). Elsevier Ltd: 982–92. doi:10.1016/j.cemconcomp.2012.06.003.
- Prud, E, P Michaud, E Joussein, C Peyratout, A Smith, and S Rossignol. 2011. “In Situ Inorganic Foams Prepared from Various Clays at Low Temperature.” *Applied Clay Science* 51 (1–2). Elsevier B.V.: 15–22. doi:10.1016/j.clay.2010.10.016.

- Purdon, A. (1940) The action of alkalis on blast furnace slag. *Journal of the Society of Chemical Industry*. 59, 191–202. in: A. Palomo, P. Krivenko, E. Kavalerova, O. Maltseva, A review on alkaline activation : new analytical perspectives, 64 (2014).
- R. Ghosh et al. 2013. "Fly-Ash Geopolymer Concrete as Future Concrete" 6 (3): 260–71.
- Rickard, William D A, and Arie Van Riessen. 2014. "Performance of Solid and Cellular Structured Fly Ash Geopolymers Exposed to a Simulated Fire." *Cement and Concrete Composites* 48. Elsevier Ltd: 75–82. doi:10.1016/j.cemconcomp.2013.09.002.
- R. Feret, Slags for the manufacture of cement, *Rev Mater Constr Trav Publish* (July 1939), in D.M. Roy, Alkali-activated cements Opportunities and challenges, 29 (1999) 249–254
- Sanjayan, Jay G, Ali Nazari, Lei Chen, and Giang Hoang Nguyen. 2015. "Physical and Mechanical Properties of Lightweight Aerated Geopolymer." *Construction and Building Materials* 79. Elsevier Ltd: 236–44. doi:10.1016/j.conbuildmat.2015.01.043.
- Shi, Caijun et al. 2006. *Alkali Activated Cements and Concretes*.
- Strozi, Marcelo, Paolo Colombo, and Márcio Raymundo. 2014. "Geopolymer Foams by Gelcasting." *Ceramics International* 40 (4). Elsevier: 5723–30. doi:10.1016/j.ceramint.2013.11.011.
- Vaou, V, and D Panias. 2010. "Thermal Insulating Foamy Geopolymers from Perlite." *Minerals Engineering* 23 (14). Elsevier Ltd: 1146–51. doi:10.1016/j.mineng.2010.07.015.
- V.D. Glukhovskiy, Soil Silicates, Gosstroizdat Publishers, Kiev, Ukraine, 1959. in: D.M. Roy, Alkali-activated cements Opportunities and challenges, 29 (1999) 249–254.
- V.D. Glukhovskiy, Ancient, modern and future concretes, in: P.V. Krivenko (Ed.), Alkaline Cements and Concretes, Proceedings of the 1st International Conference, VIPOL Stock Co., Kiev, Ukraine, 1994, pp. 1–9. in: D.M. Roy, Alkali-activated cements Opportunities and challenges, 29 (1999) 249–254. 4, ABI Books Pvt. Ltd., New Delhi, India, 1993, pp. 84–117.
- Wang, Shao-dong, and Karen L Scrivener. 1995. "Hydration products of alkali activated slag cement" 25 (3): 561–71.
- Yang, k et al. 2013. "Production and Properties of Foamed Reservoir Sludge Inorganic Polymers." *Cement and Concrete Composites* 38. Elsevier Ltd: 50–56. doi:10.1016/j.cemconcomp.2013.03.017.
- Zahra abdollahnejade. 2016. "Development of Foam One-Part Geopolymers," no. July.
- Zhang, Lianyang, Saeed Ahmari, and Jinhong Zhang. 2011. "Synthesis and Characterization of Fly Ash Modified Mine Tailings-Based Geopolymers." *Construction and Building Materials* 25 (9). Elsevier Ltd: 3773–81. doi:10.1016/j.conbuildmat.2011.04.005.
- Zhang, Zuhua, John L Provis, Andrew Reid, and Hao Wang. 2014. "Geopolymer Foam Concrete : An Emerging Material for Sustainable Construction." *Construction and Building Materials* 56. Elsevier Ltd: 113–27. doi:10.1016/j.conbuildmat.2014.01.081.
- Zhu, Mengguang, Ru Ji, Zhongmin Li, Hao Wang, Lili Liu, and Zuotai Zhang. 2016. "Preparation of Glass Ceramic Foams for Thermal Insulation Applications from Coal Fly Ash and Waste Glass" 112: 398–405. doi:10.1016/j.conbuildmat.2016.02.183.