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## **A REVIEW ON MINERAL WASTE FOR CHEMICAL-ACTIVATED BINDERS: MINERALOGICAL AND CHEMICAL CHARACTERISTICS**

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**Abstract:** This review discusses the potential of alkali-activated materials obtained from mineral waste. A brief historical background on alkali-activated materials is presented. Recent advances in the development of binders obtained from mineral wastes and alkali-activated solutions are described. The scope of this state of the art review is to identify current knowledge in support that mineral waste can be used for the production of alkali-activated binders. In addition, this review identifies the chemical activators that can be effectively utilized for such purposes in the age when wastes are still viewed by industry as disposable. Some mineral wastes which are discussed can be viewed as a new resource for recycling and recovery which will offer important economic and social benefits.

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**Keywords:** *mineral waste, mining waste, alkali-activated materials, alkaline solutions, chemical composition*

### INTRODUCTION

Recent research (McLellan et al., 2011; Turner & Collins, 2013), has stated that the CO<sub>2</sub> production due to OPC industry is approximately 5-7% of global CO<sub>2</sub> emissions, considering a range between 0.66 and 0.82 kg of CO<sub>2</sub> for every manufactured

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kilogram of Portland cement (PC); according to those studies, the comparison between OPC and alkali-activated concrete manufacturing cycles, taking into account all the processes from the raw material supplies to the final compounds, shows that the CO<sub>2</sub> impact of the latter is only 9% less than PC. However, the conclusions of the latter academic study must be interpreted with caution due to the bias coming from the inefficient mix design, heat curing the samples and precursor supply being based on fly ash derived from brown coal; an inefficient energy source. Another issue when interpreting academic studies evaluating the energy saving of alkali-activated concretes is that very few studies make reference to an application or take care to specify an appropriate reference concrete. The majority are comparing to a CEM I concrete which, is an unrealistic benchmark in the modern use of concrete.

However, there is a growing demand to replace PC concrete by alkali-activated concrete. These innovative construction materials under certain conditions have lower greenhouse gas emissions, environmental impacts and CO<sub>2</sub> emission associated with their manufacture (Provis & Van Deventer, 2009). Alkali-activated binders have either amorphous or nanocrystalline microstructures. This depends on the amount of aluminosilicate content in the precursor materials and on the mineralogical nature mineralogy of raw materials. As well it depends on the alkalinity of activating solution and on the curing conditions (Criado et al., 2010; Rahier et al., 1996; Phair & Van Deventer, 2002). In the literature, most of the studies of alkali activated materials (AAMs) are bound to the use of only a few precursor materials such as blast furnace slag (Burciaga-Díaz et al., 2013; Fernández-Jiménez et al., 1999; Türker et al., 2016), metakaolin (Alonso & Palomo, 2001; Lizcano, et al., 2011), and fly ash (Chen, et al., 2010; Criado et al., 2010). However, other, non-conventional alumina-silicate rich materials can also be used as precursors in the production of alkali-activated materials such as tungsten mining waste (Castro-Gomes, et al., 2012), glass waste (Redden & Neithalath, 2014), blends of mining waste and milled glass waste (Kastiukas et al., 2016), ceramic waste (Reig et al., 2013), and fluid catalytic cracking atalyst residue (Rodriguez et al., 2013). In order for such materials to become precursors for alkaline activation, a chemical activator is required to initiate the reaction though some are only partially reactive. Such alumina-silicate precursor materials can be activated by a host of different types of chemical activators, many of which will be discussed in this review.

#### HISTORICAL BACKGROUND OF ALKALI-ACTIVATED MATERIALS

The use of alkaline activators to stimulate the latent pozzolanic properties of materials has a long history, with some of the oldest records coming from the time of Nebuchadnezzar II (634-562 BCE) (Roy, 1999). Since October 1908 the German cement chemist and engineer H. Kühl, invented certain new and useful improvement in “slag cement and process of making the same” (Kühl, 1908). H. Kühl used in his investiga-

tion an alkali source to initiate a reaction with an alumina- and silica-containing solid precursor, to produce a solid material comparable to hardened PC (Provis & Van Deventer, 2014). Advancements in using alkali-activated cement historically started with Purdon in the 1940s (Provis & Van Deventer, 2009; Pacheco-Torgal et al., 2008a; Roy, 1999). Purdon in his investigation prepared chemically activated materials by a combination between blast furnace slag as precursor and sodium hydroxide as an activating solution. The author found that the process of the reaction was developed in two steps: first, the liberation of silica and aluminium along with calcium hydroxide takes place. Then, in the second phase, the formation of silica and alumina hydrates would happen as well as the regeneration of the alkali solution. Also, Purdon concluded that the alkali hydroxide activator acted as catalysts, having proved that statement since leaching of alkali hydroxides occurred in the same amount as presented in the original mixture (Pacheco-Torgal et al., 2008a).

Research into alkali-activated cement continued throughout the last century, by the former Soviet Union, Scandinavia, and Eastern Europe (Pacheco-Torgal et al., 2008a; Pacheco-Torgal et al., 2008c; Roy, 1999). The discussion about the history of chemically-activated binders and their most significant outcomes is summarised in table 1 (Pacheco-Torgal et al., 2008a; Palomo et al., 2014; Roy, 1999). Ancient Romans and Egyptians produced a composition of alumina-silicate calcium hydrates similar to the ones of PC and also crystalline phases of analcites, the durability of which was determined to be similar to that of natural rock (Pacheco-Torgal et al., 2008a). Later in 1957, Glukhovskiy developed a new type of binder that was obtained from alumina-silicate mixed with industrial wastes rich in alkalis named "soil-cement". The name came from the fact that the form and aspect of this new material was like a ground rock, while also possessing a cementitious capacity (Alonso & Palomo, 2001; Pacheco-Torgal et al., 2008b; Shi & Fernández-Jiménez, 2006).

Depending on the composition of the starting materials, alkali-activated binders can be divided into two groups:

a) Alkaline earth binding systems:  $\text{Me}_2\text{O}-\text{MeO}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ , the typical example of this group is alkali-activated blast furnace slag cement.

b) Alkaline binding system:  $\text{Me}_2\text{O}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ , the typical example of this group is alkali-activated metakaolin or fly ash cement (Shi & Fernández-Jiménez, 2006).

Glukhovskiy (1981) classified the alkaline activators in six groups, where M is an alkali ion: alkalis, MOH; weak acid salts,  $\text{M}_2\text{CO}_3$ ,  $\text{M}_2\text{SO}_3$ ,  $\text{M}_3\text{PO}_4$ , and MF; silicates,  $\text{M}_2\text{O} \cdot n\text{SiO}_3$ ; aluminates,  $\text{M}_2\text{O} \cdot n\text{Al}_2\text{O}_3$ ; aluminosilicates,  $\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot (2-6) \text{SiO}_2$  and strong acid salts,  $\text{M}_2\text{SO}_4$ .

Following a series of frequent fires in Europe, the scientists had to develop a material that was able to resist such attack. Thus, in the 1970s the French scientist and engineer Prof. Joseph Davidovits developed a class of solid materials synthesised by the reaction of an alumina-silicate powder with an alkaline solution, naming them "Geo-

polymers” (Davidovits, 2008; Provis & Van Deventer, 2009). These new materials had the ability to transform and polycondense like "polymers" because they are inorganic, hard and stable at high temperature and also inflammable. The polymerization process involves a chemical reaction under highly alkaline conditions on Al–Si minerals yielding polymeric Si–O–Al–O bonds with the empirical formula  $Mn[-(Si-O_2)_z-Al-O]_n \cdot wH_2O$ , where n is the degree of polymerization, z is 1, 2 or 3, and M is an alkali cation, such as potassium or sodium generating different types of poly(sialates) (Heah et al., 2012; Pacheco-Torgal et al., 2008a, 2008c; Yusuf et al., 2014).

Table 1. Research activities regarding alkali-activated based binders between 1908 to 1990 (first 82 years). (adapted from Pacheco-Torgal et al., 2008a; Palomo et al., 2014; Roy, 1999).

Author	Year	Significance
Kühl	1908	slag cement and process of making the same
Kühl	1930	Slag setting in the presence of dry potash
Chassevent	1973	Slag reactivity measurement using a dry potash and soda solution
Feret	1939	Slags used for cement
Purdon	1940	Alkali-slag combinations
Glukhovskiy	1959	Theoretical basis and development of alkaline cement
Glukhovskiy	1965	First called “alkaline cements” because natural substances used as components
Davidovits	1979	“Geopolymer” term
Malinowski	1979	Ancient aqueducts characterized
Forss	1983	F-cement (slag-alkali-superplasticizer)
Langton and Roy	1984	Ancient building materials characterized
Davidovits and Sawyer	1985	Patent of “Pyrament” cement
Krivenko	1986	D.Sc. thesis, $R_2O-RO-SiO_2-H_2O$
Malolepsy and Petri	1986	Activation of synthetic melilite slags
Malek. et al.	1986	Slag cement-low level radioactive wastes forms
Davidovits	1987	Ancient and modern concretes compared
Deja and Malolepsy	1989	Resistance to chlorides shown
Kaushal et al.	1989	Adiabatic cured nuclear wastes forms from alkaline mixtures
Roy and Langton	1989	Ancient concretes analogs
Majundar et al.	1989	$C_{12}A_7$ – slag activation
Talling and Brandstetr	1989	Alkali-activated slag
Wu et al.	1990	Activation of slag cement

Pavel Krivenko obtained concrete by alkali-activated slag and studied their physical and mechanical properties. Such research work was published in 1986 (Palomo et

al., 2014). In 1999 Palomo et al. (Palomo et al., 1999), published the first article under the title: "Alkali-activated fly ashes: A cement for the future", investigating the possibility of producing new cement using fly ash the waste resulting from coal-fired power plants. C. Shi in conjunction with P. Krivenko and D. Roy (Shi et al., 2006) published the first book which reviewed and summarised worldwide research advances in alkali-activated cement and concrete in 2006. Therefore, in 2014 J. Provis and J. Van Deventer (2014), presented a state of the art report about alkali-activated materials. The report had been prepared by the RILEM Technical Committee on Alkali-Activated Materials (TC 224-AAM).

Table 1 and 2 summarises the research activities regarding alkali-activated based binders between 1908 to 1990 (first 82 years) and last 25 years, respectively.

Table 2. Research activities regarding alkali-activated based binders between 1991 to 2014 (last 25 years). (adapted from Pacheco-Torgal et al., 2008a; Palomo et al., 2014; Roy, 1999)

Author	Year	Significance
Roy et al.	1991	Rapid setting alkali-activated cements
Roy and Silsbee	1992	Alkali-activated cements: an overview
Palomo and Glasser	1992	CBC with metakaolin
Roy and Malek	1993	Slag cement
Glukhovskiy	1994	Ancient, modern and future concretes
Krivenko	1994	Alkaline cements
Wang and Scrivener	1995	Slag and alkali-activated microstructure
Krivenko	1986	Principles governing system $\text{Me}_2\text{O}-\text{MeO}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{Al}_2\text{O}_3$ properties; proposal for the generic name "alkaline cements" and the specific name "geocement"
Palomo	1999	Production of hardened cementitious materials from alkali-activated type F fly ashes
Shi & Krivenko & Roy	2006	First book on alkali-activated cements
Provis & Van Deventer	2014	Alkali-activated materials state of the art Report. RILEM TC 224-AAM

## ADVANCES IN BINDER DEVELOPMENT: NON-CONVENTIONAL MINERAL WASTE

Recently, research studies and applications of alkali-activated materials have concentrated on the use of non-conventional mineral waste such as mining waste, waste grounded glass, incineration products obtained from sewage sludge, and mineral wools. The chemical composition of novel precursors used in the production of alkali-activated materials is rich in alumina or silicates which are the main compounds in

alkali-activated materials. The chemical compositions of these non-conventional mineral waste are shown in Table 3. Large quantities of waste resulting during the production process are disposed of in the open air causing a serious environmental impact. Thus, researchers investigate how to reuse this type of waste in the building and construction industry. The availability and predominant elements of key waste materials are presented in Table 4. The physical characteristics of novel precursors and the materials derived from them are described in this section. These novel precursors are ordered in terms of the amount generated (from the highest to the lowest quantity).

## MINERAL PROCESSING TAILINGS

### COAL GANGUE

Coal gangue is one of the major solid reject materials (Xiao & Liu, 2010). It is produced during excavation and washing of coal mines. It is a complex industrial solid waste. The major mineralogical constituents of coal gangue are illite, quartz and kaolinite. They are present as flakes of scaly morphology with a partial wormlike structure. Its major chemical composition is  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  (Cao et al., 2016; Wang et al., 2015). The presence of major quantities of coal gangue in the large area can cause many serious environmental problems (Cao et al., 2016). Calcined coal gangue with high amorphous alumino-silicate content can be used to prepared alkali-activated materials. Recent studies have shown that the compressive strength of alkali-activated materials obtained by combining sodium silicate activator and calcined coal gangue precursor at  $90^\circ\text{C}$  curing conditions for 24 h can reach about 42.5 MPa (Provis et al., 2015).

### MINE TAILINGS

In Europe, the activities of mining and quarrying generate approximately 55% of total industrial wastes according to (Eurostat, 2016). Thus, the waste generated from mining and quarry industry accumulated in large deposits present a potential risk of environmental pollution and cause serious landscape impacts. The storage of these wastes directly on land may lead to various environmental issues (Castro-Gomes et al., 2012). Different mine tailings were used in various studies as precursors for alkali-activation. Among those studied are the following: tungsten mining mud waste (Pacheco-Torgal et al., 2008d), vanadium tailing (Jiao et al., 2013), copper mine tailings (Sun et al., 2014), iron ore tailing (Duan, et al., 2016), and chromite ore processing residue (Sun et al., 2014). The following mine wastes in this section are also ordered due to their amount generated (from the highest quantity to the lowest quantity).

#### IRON ORE TAILING

Iron Ore Tailing (IOT) is an industrial waste produced in larger quantities during the process of iron extraction. The large amount of iron ore tailing accumulation represents a serious danger to human existence, due to serious pollution and occupation of soil. IOTs can be used as building materials after several grinding stages. IOT chemical composition is close to that required for ceramic materials used in construction (Zhang et al., 2006). A. Kuranchie et al. (2014) also presented a methodology of how to make eco-friendly and cost-effective bricks from IOT and activated using silicate as an alkaline solution. For the optimum curing conditions (temperature and time) and optimum activator content, the unconfined compressive strength of this bricks achieved results exceeding 50.5 MPa.

#### COPPER MINE TAILING

A considerable amount of tailing waste is generated during the processing of Cu, and Co pyrite ores (Michael Owor et al., 2007). Copper mine tailings (CMT) contain metalliferous materials. S. Ahmari and L. Zhang (2012), have investigated the feasibility to produce eco-friendly bricks based on alkali-activation technology. These authors used in their investigation a mixture of (CMT) and sodium hydroxide as an activator solution to prepare alkali-activated brick samples. The best results from this study were obtained at the optimum curing temperature of around 90 °C and in accordance to ASTM requirements. The compressive strength of the alkali-activated brick samples ranged from 3.69 to 33.7 MPa, depending on the concentration of alkaline activator solution, initial water content, forming pressure and curing temperature.

#### TUNGSTEN MINE TAILING

Tungsten tailing is waste generated from a tungsten mine. It can lead to environmental risk, like contamination of soil, pollution of water and air in the surrounding areas (Bob Wilson & Brian Pyatt, 2006). The processing industries of tungsten lead to possible adverse health effects for humans because tungsten and some of its compounds have low solubility (Kraus et al., 2001). According to Castro-Gomes et al. (Castro-Gomes et al., 2012), the mineralogy of tailings from Panasqueira tungsten mining waste was found to be mainly quartz and muscovite. F. Pacheco-Torgal et al. (Pacheco-Torgal et al., 2009), in their initial study, obtained alkali-activated materials using tungsten mine mud waste (TMWM) mixed with minor quantities of calcium hydroxide, NaOH and waterglass solutions. Prior to mixing, the mud was subject to a thermal treatment at 950°C during 2 h. Alkali-activated concrete was obtained from a mixture of limestone aggregates (aggregate/binder ratio =1.5). In turn, the alkali-activated binder consisted of a mix of tungsten mine waste mud and 10 % of Ca(OH)<sub>2</sub> with an alkaline activator (NaOH), having a concentration of 20 M. The H<sub>2</sub>O/Na<sub>2</sub>O molar ratio was 10,8. For this combination, they obtained an alkali-activated concrete

compressive strength of  $f_{c(56)} = 65,3$  MPa at 56 days curing. Recently, G. Kastiukas et al. (2016) obtained a new alkali-activated binder where 20% of the tungsten mining waste was replaced by milled glass powder to increase the overall  $\text{SiO}_2$  content. The compressive strength of alkali-activated tungsten mud waste and milled glass waste binder was 22 MPa after 28 days curing.

#### CHROMITE ORE PROCESSING RESIDUE

Chromite ore processing residue (COPR) is an industrial solid waste, produced in high lime chromium salt production process using chromite (Sun et al., 2014). The chromite ore processing residue affects a high environmental impact, also health risk with persistent of Cr(VI) leaching (Du et al., 2012). However, this waste has a high toxicity and listed as a hazardous waste produced by the chromic salts production process and contains a small portion of leached Cr(VI), (Huang et al., 2016). The authors prepared alkali-activated material by mixing blast furnace slag (BFS) with chromite ore processing residue as precursors, obtained from a chemical plant, and (NaOH) as an alkaline activator solution. alkali-activated materials were cured at of 25 °C and 90% relative humidity for 24h. The study was based on using the deferent amount of chromite ore processing residue (10, 20, 30, 40, 50, 60, 70 %) and follow-up the impact of the variations in percentages of chromite ore processing residue on the compressive strength. They found out that compressive strength varies from 44.18 MPa (10% COPR) to 13.41 MPa (70% COPR). In this study, the increase in the percentages of chromite ore processing residue had negative effects on the compressive strength.

#### VANADIUM MINE TAILING

Vanadium is an important element, extracted as a by-product. Thus, this metallic element is never found in its pure state and is one of the rare earth elements. Vanadium is used mainly to produce certain ferrous and non-ferrous alloys (Moskalyk & Alfantazi, 2003; Zhang et al., 2011). It occurs in combination with over 50 different minerals such as carnotite, roscoelite, vanadinite, mottramite and patronite (Moskalyk & Alfantazi, 2003). Extracting 1 tonne of vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) generates 120–150 tonnes of tailings. Without proper practice, management of the vanadium tailing may incur high costs and environmental pollution. Vanadium tailings contain reasonable amounts of Si and Al, which is the prerequisite of synthesizing alkali-activated materials. Nonetheless, the amorphous component of the vanadium tailings is very low, as it consists mainly of quartz. The amount of the reactive Al played an important role in the aluminosilicate gel formation (Fernández-Jiménez et al., 2006).

Jiao et al. (Jiao et al., 2013), made an alkali-activated paste by a mixture of class F fly ash and vanadium mine tailings as precursors and solid sodium silicate as an alkaline activator. The paste was cured at room temperature (28 °C). These authors



suggested that the vanadium tailings possessed the potential for the synthesis of fire-resistant alkali-activated products, according to the results obtained from the study. In this study, the compressive strength was not given by the authors.

#### RED MUD

A one-part alkali-activated material was synthesized from alkali–thermal activated Bayer red mud (Gräfe et al., 2011; Hind et al., 1999; Ye et al., 2016). In refining bauxite by smelting alumina ( $\text{Al}_2\text{O}_3$ ) the chemist autrichien “Karl Josef Bayer” developed and patented a process named the “Bayer Process”. Thus, the process became the fundamental method of industrial production of aluminium in the world (Hind et al., 1999). The Bayer Process used a digestion method process for the raw material (bauxite ore) using caustic soda, the residue of which was called “Bayer Red Mud” (RM) or “bauxite residue”. This waste possesses a high alkalinity of  $\text{pH } 11.3 \pm 1.0$  (Gräfe et al., 2011; Hind et al., 1999; Ye et al., 2016). Land disposal of RM may cause a serious environmental impact since its infiltration into the surrounding environment poses environmental and health issues. RM is classified as a toxic industrial waste (Gelencsér et al., 2011; Hind et al., 1999) and ecological disasters caused by the collapse of RM dams have occurred on several occasions in the past. Some research studies have been carried on to produce alkali-activated materials from RM. Due to its low reactivity and low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio ( $<2.0$ ) (Dimas et al., 2009; Ye et al., 2016), it has been combined with other higher grade precursors such as metakaolin. N. Ye et al. (2016), used red mud and metakaolin to prepare alkali-activated materials using sodium hydroxide (NaOH) and sodium silicate as alkaline activators solutions. The authors obtained 10.8 MPa compressive strength after 28 days curing.

#### INCINERATED BOTTOM ASH

Incinerated bottom ash (IBA) represents the major portion of the solid residue from the combustion process of municipal solid waste (Jurič et al., 2006). IBA has been reutilised in several civil engineering applications. According to current state-of-the-art, IBA has so far been used for application such as road, embankment and, pavement construction and also as aggregate and filler for concrete. However, nowadays several research authors are using IBA as a new alkali-activated precursor. Chen et al. (2016) activated IBA with sodium hydroxide and sodium silicate solution to synthesise an aerated alkali-activated material with low density. Garcia-Lodeiro (2016), used IBA and fly ash to manufacture hybrid cements. The hybrid cement was developed by blending 60 % PC clinker and 40 % incinerated bottom ash and fly ash. It exhibited satisfactory 28-day mechanical strength (upward of 32.5 MPa).

### WASTE GLASS

Every year millions of tonnes of waste glass are generated from municipal waste streams all over the World (Torres et al., 2009). Until now, there are different types of waste glass that have been used in the production of alkali-activated materials, such the following: industrially manufactured waste glass (Kastiukas et al., 2016), solar panel waste glass (Hao et al., 2013), and glass powder cullet (Vafaei & Allahverdi, 2016). Milled waste glass powder is rich in silica and can be used as a source of reactive silica in the preparation of alkali-activated materials (Pascual et al., 2014; Novais et al., 2016). Pascual et al. (2014), found that the activation of glass with metakaolin in the presence of 5M sodium hydroxide solution revealed the presence of calcium silicate and sodium silicate hydrate (C(N)-S-H) type gel while in the presence of MK, both C-S-H and N-A-S-H are present, the presence of N-A-S-H type gel due to the addition of MK, allows the stabilization of alkali ions, these authors also said that the advantage of glass powder that this material can be used several times without significant changes in its chemical and physical properties. Torres-Carrasco et al. (2015), used waste glass as an alkaline activator (waterglass family), which proved that waste glass is a viable substitute for the waterglass commonly used to prepare alkali-activated materials. Others authors (Wang et al., 2016) studied the engineering properties of alkali-activated waste glass material by using waste LCD glass sand to replace the slag with deferent percentages (0%, 10%, 20%) to produce mortar. The slump flow increased with the increased replacement by glass sand, along with the compressive strength.

### PALM OIL FUEL ASH

Palm oil is the most used vegetable oil in domestic homework like cooking and food processing, in oleochemicals, cosmetics and also in fuel (Oosterveer, 2015). Mijarshet et al. (2014), ground palm oil fuel ash (POFA) in a ball mill to obtain particle sizes of about 10  $\mu\text{m}$ . This palm oil fuel ash was heated at 500  $^{\circ}\text{C}$  for 1 h to remove the unburned carbon. Then the palm oil fuel ash was subjected to a second stage of grinding to obtain treated palm oil fuel ash (TPOFA). The chemical composition of the TPOFA used in his study is provided in Table 3. Ariffin et al. (2013), used untreated palm oil fuel ash in combination with pulverised fuel ash (PFA) with a composite alkaline activator of sodium hydroxide (NaOH) and sodium Silicate ( $\text{Na}_2\text{SiO}_3$ ) to produce alkali-activated materials. They achieved a compressive strength of 30 MPa after 28 days curing. According to another study carried on by Khankhaje et al. (2016), it was concluded that the addition of original palm oil fuel ash (OPOFA) to concrete as partial replacement of cement increased the compressive strength. This is explained by the low pozzolanic reactivity and high water demand of original palm oil fuel ash that reduce the workability and strength of palm oil fuel ash concrete.

## WASTE GROUND COFFEE

Coffee is one of the most popular traded products worldwide. In terms of global trade, it is the second most traded product. A large amount of coffee by-products or residues are generated during its processing. To convert the raw coffee fruit into liquid, there are two basic methods of coffee processing: Wet method and dry method (Murthy & Madhava Naidu, 2012). The authors (Eliche-Quesada et al., 2011), used raw clay and waste ground coffee ash to produce a clay brick. Samples were prepared by mixing clay and coffee waste ash with different percentages. These samples were cured in typical curing condition for manufacturing clay bricks. The blend containing of clay and 3% of coffee waste ash presented the best compressive strength results of about 70MPa. Also, it was found out that the incorporation of coffee ground amounts up to 5% causes an increase in total porosity of the clay.

## INCINERATED SLUDGE PRODUCTS

### WASTE PAPER SLUDGE

Waste paper sludge is a by-product derived from effluent treatment processes. Several thousand tonnes of waste paper sludge are generated annually (Yan et al., 2011). In the EU alone, about 6 million tonnes of waste are generated annually. There have been many studies focusing on reusing paper sludge in construction materials. Such studies are mostly based on ordinary PC. Many of these studies reported problems with using waste paper sludge in concrete, such as increased drying shrinkage and water absorption which leads to a reduction in compressive strength (Yan & Sagoe-Crentsil, 2012). Yan and Sagoe-Crentsil used waste paper sludge to produce alkali-activated materials. The sludge was oven dried first at 110 °C for 48 h and later blended with fly ash. The alkali-activating solution consisted of NaOH and sodium silicate solution. They found out that mortar samples with a paper sludge content up to 10% and cured up to 91 days achieved a compressive strength of 31.2 MPa. Others authors (Antunes Boca Santa et al., 2013), used calcined paper sludge after heat treatment blended with IBA. Again sodium hydroxide and sodium silicate were used as alkaline activators. In this case, the compressive strength results of the alkali-activated samples were about 10-25 MPa.

### WATER TREATMENT SLUDGE

Water Treatment Sludge (WTS) is a solid waste by-product generated in water treatment plants, as an output from the processing of drinking water and also extracted from raw water by coagulation techniques (Keeley et al., 2012). Nimwinya et al. (2016), developed a lightweight alkali-activated binder using calcined water treatment sludge (WTS) and rice husk ash (RHA) blends as a sustainable precursor, and they use a mixture of sodium hydroxide (NaOH) and sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) as an alkaline

activators solution. Samples were cured both at room and higher temperatures (60°C). A compressive strength of 22 MPa was obtained from samples containing 50% WTS and 50% RHA). In another study, (Suksiripattanapong et al., 2015) used WTS and fly ash as the precursors. The liquid alkaline activator was a mixture of sodium silicate solution ( $\text{Na}_2\text{SiO}_3$ ) and sodium hydroxide solution (NaOH). Samples obtained a 7-day compressive strength of about 14 MPa after curing at 75°C.

#### MINERAL WOOLS

Mineral wools are the most common insulation materials in the world. Just in the EU, the total mineral wool waste is currently over 2.3 Mt annually. Mineral wool waste can be divided into two types: rock wool (RW) and glass wool (GW) (Kinnunen et al., 2016; Papadopoulos, 2005). This material is classified as unrecyclable waste because of its fibrous nature and low density. Regarding the chemical composition, rock wool contains about 40% silicon dioxide ( $\text{SiO}_2$ ) while glass wool contains about 62%. They both contain other constituents like CaO,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in considerable proportions as reported by (Yliniemi et al., 2016). These authors used mineral wools as precursors for alkali-activated materials without any additional co-binders with a sodium aluminate solution in heat curing conditions. They obtained different alkali-activated materials with different compressive strengths for both RW (~30.0 MPa) and for GW (~48.7 MPa). Other authors (Kinnunen et al., 2016), used rock wool waste blended with fly ash to obtain alkali-activated composites, after heat treatment and curing at room temperature. They obtained a compressive strength of 12 MPa for alkali-activated materials synthesised with 33 % rock wool and 47 % fly ash.

#### FLUID CATALYTIC CRACKING CATALYST RESIDUES

The fluid catalytic cracking catalyst residue (FCC) is obtained as a by-product from the petroleum industry. This material is also classified as an aluminosilicate source for the production of alkali-activated binders. The fluid catalytic cracking catalyst used in petroleum cracking process contains largely spherical or spheroidal shape particles. Its diameter ranges from 100 to 20  $\mu\text{m}$  (Payá et al., 1999; Tashima et al., 2013). In the study of Tashima et al. (Tashima et al., 2012b), they conclude that FCC is an inorganic industrial waste that can be used for preparing alkali-activated materials. Binders and mortars were obtained by FCC and NaOH/waterglass blends and cured at 65 °C. The obtained compressive strength was in the range between 8.52 to 68.34 MPa.

#### RICE HUSK–BARK ASH

The rice husk–bark ash (RHBA) is a solid waste produced by burning a mixture of rice husk (65% by weight) and eucalyptus bark (35% by weight) as fuel by the

fluidized bed combustion process in a biomass power plant. The major chemical constituent of RHBA is  $\text{SiO}_2$  (about 75%), the amorphous silica in rice husk ash contained in (65 %  $\text{SiO}_2$ ) can be used as pozzolanic materials. This is due to the high reactivity of RHBA (P. Chindaprasirt, Homwuttivong, & Jaturapitakkul, 2007; Nazari, Bagherim, & Riahi, 2011; Sata et al., 2007). Nazari et al. (2011), in their study obtained alkali-activated materials from a blend of 60 % RHBA and 40 % fly ash activated with waterglass and sodium silicate. The ratio between precursors and alkali activator solution was 0.4, and the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio was 3.81. The compressive strength of the samples cured at room temperature for 7 days was 27 MPa.

#### SILICOMANGANESE (SiMn) SLAG

Slags result from steel industries using electric arc furnace technology. Silicomanganese (SiMn) slag is a by-product generated during production of the silico-manganese alloy by carbothermic reduction of raw materials by electric arc furnace (Frias et al., 2006; Kumar et al., 2013). SiMn slag has high manganese content if compared with the traditional slag from the blast furnace, which has been accumulating in the environment for many years, but the total global inventory of SiMn slag is much higher (Frias et al., 2009; Frias et al., 2006). Kumar et al. (2013), developed an alkali-activated cement from mechanically activated silico-manganese (SiMn) slag. Its main constituents were  $\text{SiO}_2$ , CaO and  $\text{Al}_2\text{O}_3$  which comprised 80% of the total composition. It also contained MnO and MgO in a significant amount. The authors obtained alkali-activated cement pastes by mixing high-energy milled silico-manganese slag with sodium hydroxide as an activator. The compressive strength was 101 MPa after 28 days of sealed curing at  $27 \pm 2$  °C.

#### CERAMIC WASTE

The construction and manufacturing sectors are the main fields generating ceramic wastes; approximately 45% of construction and demolition wastes are ceramic. Depending on the source of raw materials, ceramic can be grouped in three categories, namely structural ceramic products, ceramic tiles and stoneware (Stock, 2014). Reig et al. (2013), presented a study about alkali-activation of ceramic waste materials. The authors used two types of ceramic waste materials in the alkaline activation; red clay brick and porcelain stoneware as the precursor, and sodium hydroxide (NaOH) as an activator solution. The specimens achieved a compressive strength in the range of 29 to 41 MPa depending on the (water/binder) ratio and activator/binder ratio. The addition of  $\text{Ca}(\text{OH})_2$  was not necessary to prepare and make alkali-activated mortars using porcelain stoneware. In this case, the compressive strength was about 30 MPa after 7 curing days at 65 °C.

Table 3. Chemical composition of mineral waste used to produce alkali-activated materials.

Types of waste		Chemical Composition (%)													References
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	MnO	CaO	TiO <sub>2</sub>	K <sub>2</sub> O	MgO	P <sub>2</sub> O <sub>5</sub>	So <sub>3</sub>	Others	LOI*	
Mineral Processing tailings	Coal gangue	39,1	31,06	9,48	0,16	-	0,38	0,98	0,26	0,24	-	-	-	26,6	(Cao et al., 2016)
	Iron Ore	34,7	16,22	12,3	0,54	0,13	7,63	0,3	1,52	8,92	-	-	-	13,2	(Duan et al., 2016)
	Copper	64,8	7,08	4,33	0,9	-	7,52	-	3,26	4,06	-	1,66	-	-	(Ahmari & Zhang, 2013)
Incinerator bottom ash (IBA)	Tungsten	53,5	16,66	12,3	0,62	-	-	1,39	7,65	1,27	-	-	-	-	(Pacheco-Torgal et al., 2008e)
	Chromite ore	6,46	8,15	19,52	2,85	0,46	34,27	0,22	-	13,64	-	-	0,2	7,53	(Sun et al., 2014)
	Vanadium	64,2	10,27	4,98	5,27	-	4,46	-	2,06	-	-	-	-	1,15	(Jiao et al., 2013)
Waste glass	Red Mud	20,38	24,50	9,48	11,46	-	12,86	2,92	0,88	1,00	-	1,00	-	15,40	(Ye et al., 2016)
	Incinerator bottom ash (IBA)	32,75	8,57	10,02	2,87	0,15	29,06	1,57	1,24	1,75	4,77	3,01	-	-	(Chen et al., 2016)
Palm Oil Fuel Ash	Waste glass	72,5	0,40	0,2	13,70	-	9,70	-	0,1	3,30	-	-	-	-	(Pascual et al., 2014)
	Incineration products of sludges	61,33	7,2	5,11	0,123	0,097	8,20	0,25	6,50	4,69	4,6	0,27	1	2,53	(Mijarsh et al., 2014)
	Coffee waste	1,09	0,79	1,26	8,42	0,38	13,73	0,14	23,87	22,93	23,66	3,30	-	-	(Elliche-Quesada et al., 2011)
Mineral Wools	Waste paper sludge	7,69	6,08	0,17	0,25	-	32,3	0,15	0,05	2,62	-	-	-	52,6	(Antunes Boca Santa et al., 2013)
	Sludges resulting from water treatment	59	24,64	6,63	4,08	-	0,69	0,88	1,54	1,14	-	-	-	1,41	(Nimwinya et al., 2016)
Fluid catalytic cracking	Rock	42,0	16,6	11,3	1,6	-	14,7	09	0,5	12,2	0,1	0,03	-	2,4	(Kimmunen et al., 2016)
	Glass	62,4	1,8	0,6	16,8	-	7,1	-	0,9	2,2	-	0,9	-	5,1	(Ylmiemi et al., 2016)
Rice husk bark ash	Incineration products of sludges	46,94	48,40	0,59	0,31	-	0,11	1,20	0,02	0,17	0,01	0,02	-	0,50	(Rodriguez et al., 2013)
	Sludges resulting from water treatment	81,36	0,4	0,12	-	-	3,23	-	-	-	-	0,85	-	3,55	(Nazari, 2012)
Ceramic	Red clay brick	42,6	12,2	1,0	0,36	9,9	25,2	0,36	2,2	4,2	-	0,12	-	-	(Frias et al., 2006)
	Porcelain stoneware	50,95	16,92	6,68	0,55	-	9,92	-	4,33	5,62	-	3,37	-	1,65	(Reig et al., 2013)
	Porcelain stoneware	71,35	19,37	6,68	4,68	-	0,51	-	1,73	0,59	-	0,02	-	0,67	(Reig et al., 2013)

Table 4. alkali-activated materials from novel precursors versus availability and main composition

Types of waste	Process of production	Amount generated: tonnes/year	Predominant elements	Country	References	
Coal gangue	Excavation and washing of the coal mine	$2 \times 10^{11}$	SiO <sub>2</sub> (39.08)	China	(Li et al., 2010)	
	Residue of alumina production process (Bayer process)	$120 \times 10^6$	Fe <sub>2</sub> O <sub>3</sub> (30.9)	worldwide	(Heet al., 2013)	
Red mud	Waste from iron ore mine tailings production	$632 \times 10^6$	SiO <sub>2</sub> (57.31)	Western Australia	(Francis et al., 2014)	
	Mine tailings	The mining and processing of copper	$0.58 \times 10^6$	-	Kilimbe area (Western Uganda)	(Mwesigye et al., 2016)
		Mineral extraction and processing produce	$0.37 \times 10^6$	SiO <sub>2</sub> (53.48)	Panasqueira/ Portugal	(Pacheco-Torgal et al., 2008c)
	Chromite Ore PR	The high lime process	$0.06 \times 10^6$	CaO (34.27)	China	(Sun et al., 2014)
Mineral Processing tailings	Vanadium tailing of vanadium extraction from stone coal	extracting 1 tonne of V <sub>2</sub> O <sub>5</sub> generates 120–150 tonnes of tailing	SiO <sub>2</sub> (64.17)	China	(Jiao et al., 2013)	
	Incinerator bottom ash (IBA)	Incineration municipal solid waste	-	Taiwan	(Wu et al., 2016)	
Waste glass	disposed solid waste	$14 \times 10^6$	SiO <sub>2</sub> (60-80)	worldwide	(Siddique, 2008)	
Palm oil fuel ash	Cooking and food processing	$10 \times 10^6$	SiO <sub>2</sub> (61.33)	Malaysia	(Khanhaje et al., 2016)	
Waste glass	disposed solid waste	$14 \times 10^6$	SiO <sub>2</sub> (60-80)	worldwide	(Siddique, 2008)	
Coffee waste	treatment of coffee powders with hot water	$6 \times 10^6$	-	worldwide	(Jeguirim et al., 2014)	
	Effluent treatment processes	$4.5 \times 10^6$	TiO <sub>2</sub> (13.2)	Europe	(Yan & Sagoes-Crentsil, 2012)	
Incineration products of sludges	Waste paper sludge	$11 \times 10^4$ tons/wet S $25.6 \times 10^4$ tons/ sec S	SiO <sub>2</sub> (58.99)	Thailand	(Nimwinya et al., 2016)	
	Sludges resulting from WT					
Mineral wools	Rock	$2.3 \times 10^6$	SiO <sub>2</sub> (62.4)	worldwide	(Yiniemi et al., 2016)	
	Glass		SiO <sub>2</sub> (40.4)			
Fluid catalytic cracking	Petroleum refining processes	$0.2 \times 10^6$	Al <sub>2</sub> O <sub>3</sub> (48.40)	worldwide	(Rodriguez et al., 2013)	
Rice husk bark ash	Biomass power plants	$0.16 \times 10^6$	SiO <sub>2</sub> (81.36)	The power Plant company providing RHBA	(Nazari et al., 2011)	
silico-manganese (Si/Mn) slag	Electric arc furnace technology	$0.15 \times 10^6$	SiO <sub>2</sub> (42.6)	Spain	(Frias et al., 2006)	
	Ceramic waste	Red clay brick	SiO <sub>2</sub> (50.95)	European ceramic industry.	(Stock, 2014)	
Porcelain			SiO <sub>2</sub> (71.35)			

## ALKALI ACTIVATORS

In alkali-activated synthesis, there are various different types of alkaline solutions that have been used as activators. The most popular activator solutions used are combinations of either sodium or potassium silicate with sodium hydroxide (Provis & Van Deventer, 2009). Activating solutions play a key role in the reaction process and final binder properties (Esaifan et al., 2016; Provis & Van Deventer, 2009). The reaction begins immediately when the chemical activator is added to the raw reactive solid components. So aluminosilicate binder materials activated by alkali hydroxides or silicates under high-pH conditions are classified in general as alkali-activated materials (Provis & Van Deventer, 2009). Table 5 present the compressive strength of alkali-activated materials obtained by combinations of alkali activators with precursors (conventional and non-conventional minerals waste). In this section, we include the most commonly and widely researched alkali activators and also recently established activators which show promising results.

### ALKALI HYDROXIDE ACTIVATORS

Sodium and/or potassium are the most commonly used activators in the alkali hydroxides group. The viscosity and heat of dissolution are the most important properties of concentrated hydroxides that must be taken into consideration. There are five alkali metal hydroxides: Lithium hydroxide (LiOH), Sodium hydroxide (NaOH), Potassium hydroxide (KOH), Rubidium hydroxide (RbOH) and Caesium hydroxide (CsOH). These solutions are considered as concentrated aqueous solutions (Provis & Van Deventer, 2009).

#### LITHIUM HYDROXIDE (LlOH)

Lithium has been used as an accelerator for polymerization due to its ability to enhance the colloid formation in precipitated silica. The metal cation  $\text{Li}^+$  is also used in cement and concrete technology to optimise and minimise the degradation caused by the alkali-aggregate reaction (Provis & Van Deventer, 2009).

#### SODIUM HYDROXIDE (NAOH)

The analysis and the modelling of thermodynamic properties of NaOH solution was defined in several decades ago (Pabalan & Pitzer, 1987). This solution is the cheapest and most widely available of the alkali hydroxides. Thus NaOH is the most commonly used hydroxide activator in alkali-activated materials synthesis (Provis. & Van Deventer, 2009; Nematollahi & Sanjayan, 2014; Somna et al., 2011). For a sodium hydroxide solution with 8.0 molar concentration, the value of pH is 13.32 at 23 °C (Nematollahi & Sanjayan, 2014). According to Palomo et al. (Palomo et al., 1999), the activation of the fly ash with NaOH solution produces some hydroxysodalite together



with the minerals of the fly ash. Other authors (Alonso & Palomo, 2001; Chindaprasirt & Chalee, 2014; Chindaprasirt et al., 2009; Somna et al., 2011), also state that the compressive strength of alkali-activated concretes increases with the increase in NaOH concentration. It was found out that high concentrations of NaOH resulted in the leaching of a larger amount of Si and Al from fly ash or metakaolin (Alonso & Palomo, 2001; Chindaprasirt & Chalee, 2014; Chindaprasirt et al., 2009; Somna et al., 2011). According to the study of Chindaprasirt et al. (2014), it produced an improved degree of polycondensation and resulted in a high development of long-term compressive strength of alkali-activated concrete. They also conclude that the steel corrosion of alkali-activated concretes tended to decrease with the increasing of NaOH concentration. Besides, other authors have concluded that the compressive strength and microstructure of the alkali-activated materials pastes are dependent on NaOH concentrations (Somna et al., 2011). Alonso et al. (2001), studied the alkali activation of metakaolin with sodium hydroxide. The conclusion of his work was that the increase in activator solution concentration above 10 M induces a delay in the formation of the alkaline polymer as a consequence of reduced ion mobility. An excessive sodium hydroxide concentration provokes an increase in the concentration of dissolved species to a stage where the species diffusion in the aqueous phase is reduced.

#### POTASSIUM HYDROXIDE (KOH)

Commercial grade potassium hydroxide can be obtained in the form of pellets (97% -100% purity) like NaOH. Also, potassium hydroxide pellets can be dissolved in the required amount of water according to the desired molarity. However, when comparing between (KOH) and (NaOH) solution molarity, it was concluded that (KOH) is more alkaline than sodium hydroxide (NaOH) (Raijiwala et al., 2012). Also, zeolite formation takes place in KOH activated alkali-activated materials similar to their sodium hydroxide containing counterparts, and the crystallisation in KOH/Metakaolin is less rapid compared to NaOH/metakaolin system (Duxson et al., 2007). According to Fernández-Jiménez et al. (2006), the cation  $K^+$  has a larger size compared to  $Na^+$  and creates a regulatory role in reaction kinetics because it induces a lower crystallisation speed of the zeolites and hence a slower development of prezeolitic gel. However, the carbonation of KOH-activated alkali-activated is also a potentially problematic issue.

#### CALCIUM HYDROXIDE ( $Ca(OH)_2$ )

Calcium hydroxide has been mainly used to activate GGBFS or metakaolin to produce structural binders by the pozzolanic reaction. This activator is a practical and safe alternative to alkaline solutions because it is less expensive compared to others activators but also generates solutions with much lower pH values  $\sim 12.5$  at maximum (Jeong et al., 2016). Alonso and Palomo (2001) concluded that an increase of metakaolin proportion upon calcium hydroxide leads to the larger formation of alkaline

aluminosilicate due to the increase in reactant species dissolved. The use of  $\text{Ca}(\text{OH})_2$  instead of KOH or NaOH provides a solution to some of safety issues associated with highly alkali solutions. However, the samples made with pure  $\text{Ca}(\text{OH})_2$  results in poor mechanical properties if the aluminosilicate source has no pozzolanic properties.

#### ALTERNATIVE ACTIVATORS

##### SILICA FUME ACTIVATOR (SFA)

Silica fume activator (SFA) is a product prepared from silica fume and acts as a very effective activator (Rouseková et al., 1997). According to (Vladimír Živica, 1993), silica fume activator is more active than sodium hydroxide (NaOH) and waterglass. This conclusion was confirmed by Rouseková et al. (1997) in their investigation when preparing mixtures containing silica sand, blast furnace slag, silica fume, and alkali-silica activator or sodium hydroxide (NaOH). Živica (2006), in his investigation of alkali-activated materials, prepared mortar test specimens. Different combinations of precursors were used (Portland cement with silica sand, slag) for activation with silica fume activator. After the tests, he concluded that silica fume positively affected the intensification of C-S-H gel formation and also the heterogeneity of the pore structure.

##### THE RICE HUSK ASH (RHA)

Rice husk ash (RHA) is produced by burning rice husk material at 600 °C for 2 h. Afterwards, it is grounded to obtain a powder with a small particle size in order to get a highly reactive pozzolan. Bernal et al. (2012) found out that the content of amorphous silica in the final RHA was 68%, with an unburnt carbon content of less than 2%. These authors used RHA and NaOH analytical grade (99.9), mixed for 10 min and sealed in plastic containers immersed in a water bath at room temperature (25 °C) for 24 h, to prepare alkali rice husk ash activator (RHAA). The use of rice husk ash as alkali activator contributes to the reduction of the environmental impact of alkali-activated materials. Recently, Tchakouté et al. (2016), used the same process to obtain rice husk ash. But first, they removed the metallic ingredients to produce completely pure silica, by leaching rice husk in HCl (5 M) for 24 h. After leaching, the ash was thoroughly washed with water until neutral pH and then dried in air. The (RHA) activator improved the mechanical performance of the alkali-activated material. Also, they suggested that (RHA) has an economical technology that can be used to produce sodium waterglass, and this activator is environmentally friendly.

##### OTHER ACTIVATORS

Researchers in the last few decades have also been interested in using an alkali carbonate solution rich in calcium (Shi et al., 2006). Authors (Fernández-Jiménez et al., 2006), used the hydroxide-carbonate solution as an activator. The result is a porous

product according to the poorly reactivity with the Class F fly ashes. In the literature, there are many types of activators hydroxide-carbonate class.

#### POTASSIUM CARBONATE ( $K_2CO_3$ )

According to Esaifan et al. (2016), the use of  $K_2CO_3$  as an activator with hydrated lime  $Ca(OH)_2$  produces a high alkaline viscous gel not stable as a function of time due to the carbonation of  $Ca(OH)_2$  to form  $CaCO_3$ . The alkaline mixture  $\{Ca(OH)_2/K_2CO_3\}$  reacts with kaolinite to produce an alkali-activated material at a temperature of 80 °C, due to the presence of  $Ca(OH)_2$ , KOH in the high alkaline viscous gel. The best results of compressive strength are obtained when applying  $K_2CO_3$  as a liquid additive and  $Ca(OH)_2$  as a solid additive.

#### SODIUM CARBONATE ( $Na_2CO_3$ )

Sodium carbonate (soda ash) is an anhydrous material containing about 99 % of ( $Na_2CO_3$ ), obtained from natural sources and sustainable manufacturing processes; sodium carbonate can be divided into two groups according to their physical characteristics. The main measure of the classification is the bulk density: light and dense soda ash.

Light soda ash is produced by the recovery of carbonation towers or vacuum crystallizers called and called “recovered sodium sesquicarbonate precipitate” with a bulk density of 510 to 620  $kg/m^3$  (Shi et al., 2006). The second classification of “dense soda ash” is produced by the hydration and subsequent dehydration through calcination of light soda ash to produce denser crystals, with a bulk density of 960 to 1060  $kg/m^3$ . The two classification have the same chemical and physical properties (Shi et al., 2006). Fernández-Jiménez et al. (1999), proposed Sodium carbonate ( $Na_2CO_3$ ) as an alternative activator for GGBS to develop a more durable alkali-activated slag cement.

#### SODIUM SULPHATE ( $Na_2SO_4$ )

Sodium sulphate, also known as (disodium sulphate), comes from different natural resources. Also, is can be obtained from industrial manufacturing processes. Sodium sulphate in its natural form is found in two principal minerals: thenardite (anhydrous  $Na_2SO_4$ ) and mirabilite ( $Na_2SO_4 \cdot 10H_2O$ ). The chemical composition of thenardite contains  $Na_2O$  (43.68%) and  $SO_3$  (56.32%). However, it is a soluble material with a solubility of 15.9% by mass in water at 20 °C. Also, thenardite has pH values ranging from 6.0 to 9.0 for 1% solution. Sodium sulphate can be used as an alkaline activator for Portland cement and lime-based cementing materials (Shi et al., 2006).

Table 5. The compressive strength of alkali-activated materials from mineral waste, activators, and curing conditions.

Types of novel waste	Material added	Activators	Ratio (novel waste/ other materials)	Curing (period and environment)	Compressive strength (MPa)	References	
Mineral Processing tailings	Coal gangue (CG)	Na <sub>2</sub> SiO <sub>3</sub>	0.5(CG):0.25(S):0.25(FA)	28d/ambient	35.52	(Li et al., 2006)	
	Iron Ore (IO)	NaOH+ Na <sub>2</sub> SiO <sub>3</sub>	0.9(IO): 0.1(FA)	28d/standard condition	47	(Duan et al., 2016)	
	Mine tailings	Copper (COP)	NaOH	0.9(COP):0.1(CKD)	7d/90°C	50	(Ahmari & Zhang, 2013)
		Tungsten (Tn)	NaOH+Na <sub>2</sub> SiO <sub>3</sub>	0.9(Tn):0.1(Ch)	28d/room T°	28	(Pacheco-Torgal et al., 2008d)
		Chromite ore (CO)	NaOH and Na <sub>2</sub> S <sub>9</sub> H <sub>2</sub> O	-	2h/60°C	42	(Sun et al., 2014)
		Vanadium (V)	NaOH	0.7(V):0.3(FA)	7d/room T° 900°C	55	(Jiao et al., 2013)
	Red Mud (RM)	RHA	NaOH	0.33(RHA):0.66(RM)	49d/room T°	20.46	(He et al., 2013)
	Incinerator bottom ash (IBA)	Clinker/(IBA+FA)	Ca <sub>3</sub> O <sub>2</sub> and Na <sub>2</sub> SO <sub>4</sub>	0.6(IBA):0.0668/ 0.332) (Cl)	28d/ambient	33	(Garcia-Lodeiro, et al., 2016)
	Glass waste (GW)	Metakaolin	NaOH	0.95(GW):0.05(MK)	28d/ 20°C	22	(Pascual et al., 2014)
	Palm oil fuel ash (POFA)	Fly ash	NaOH/ Na <sub>2</sub> SiO <sub>3</sub>	0.5(POFA):0.5(FA)	28d/30°C	17.5	(Ranjbar et al., 2014)
Coffee waste (Cof)	Raw clay (Rcl)	-	0.93(Rcl):0.03(Cof)	Condition of manufacturing brick	70	(Elche-Quesada et al., 2011)	
Incineration products of sludge	Waste paper sludge (Wps)	NaOH/Na <sub>2</sub> SiO <sub>3</sub>	0.33(Wps): 0.66(BA)	28d/room T°	15	(Antunes Boca Santa et al., 2013)	
	Sludge resulting from water treatment (Sw)	Na <sub>2</sub> SiO <sub>3</sub> / NaOH	0.7(Sw):0.3(FA)	7d/75°C	14	(Suksirattapanpong et al., 2015)	
Mineral wools	Rock (Mwr)	NaOH/ NaAlO <sub>2</sub>	1(Mwr):1.43(FA)	28d/ambient	12.8	(Kinnunen et al., 2016)	
	Glass	Sodium aluminate	-	28d/22°C	05	(Yiniemi et al., 2016)	
Fluid catalytic cracking (FCC)	-	water/glass/NaOH	-	3d/65°C	68	(Tashima et al., 2012a)	
Rice husk bark ash (RHBK)	Fly ash	NaOH/ Na <sub>2</sub> SiO <sub>3</sub>	0.6(RHBK):0.4 (FA)	7d/22°C	27	(Nazari et al., 2011)	
Silico-manganese (SiMn) slag	-	NaOH	-	28d/ambient	101	(Kumar et al., 2013)	
Ceramic waste	Red clay brick	NaOH+KOH	-	28d/60°C	71.1	(Sun et al., 2013)	
	Porcelain stoneware	-	-	-	-	-	

SODIUM SILICATES ( $\text{Na}_2\text{O}\cdot\text{nSiO}_3$ )

Sodium silicates are the most water-soluble alkali silicates used in alkali-activated materials, sodium silicates are cheaper and produced in substantially larger quantities comparing with other silicates like “potassium silicates” (Davidovits, 2008). Waterglass ( $\text{Na}_2\text{O}\cdot\text{nSiO}_3$ ) contains dissolved glass that has water-like properties. Thus, they commonly used as sealants, binders and in other fields because they have excellent adherence properties, film formation and low cost (Christensen et al., 1982). Sodium silicate is used to enhance the strength of cement and concrete as well as increase the fire and acid resistance in materials (Wiley-VCH, 2005).

PHOSPHORIC ACID ( $\text{H}_3\text{PO}_4$ )

Phosphoric acid is also used as an activator in the new member family of activated materials named “phosphoric acid-activated materials” (Liu et al., 2012). The process reaction between the activator and the precursors comes from the interaction of the positive charges on the  $[\text{PO}_4]$  content in the phosphoric acid activator balanced the negative charges of the  $[\text{AlO}_4]$  content in the precursors (Le-ping et al., 2010). In recent studies, S. Louati et al. (2016) used calcined illito-kaolinitic clay at  $700^\circ\text{C}$  as a precursor and phosphoric acid ( $\text{H}_3\text{PO}_4$ ) as an activator. The resulting materials when analyse by XRD have an amorphous phase and show a presence of  $\text{AlPO}_4$  as a product of the reaction. The compressive strength of the samples was 37 MPa after 21 days of curing.

## CONCLUSIONS

Chemically activated cementitious materials are certainly an emerging technology for the utilization of industrial by-products such as fly ash and slag. However, researchers' have recognised the need to expand the range of precursor materials to include many of the other emerging and non-conventional waste materials. In addition, activators materials used in the preparation of chemically activated binders have been seen as a cause due to them commonly based on highly alkaline solutions. This study reviewed the latest types of mineral waste precursor materials which have been successfully activated to produce binders for various applications. Also, a review of the well established and recently discovered alternative chemical activators is also presented. Based on the latter findings, the following conclusions can be drawn:

- Alkali-activated materials can be successfully produced from a broad range of different mineral waste sources due to their favourable chemical composition and mineralogical nature.
- Successful blends of precursor materials include vanadium and iron ore tailings in combination with fly ash. Tungsten mining waste has shown good compatibility with calcium hydroxide and waste glass. In the same manner, palm oil fuel and rice

husk bark ashes, along with sludge incineration products resulting and mineral rock wools can be transformed into alkali-activated materials when partially blended with fly ash.

- Waste materials demonstrating good reactivity on their own have been silico-manganese slag, ceramic waste and mineral glass wools.
- Waste materials with exceptionally high levels of alumina such as fluid catalytic cracking catalyst residue (48.40 %  $\text{Al}_2\text{O}_3$ ) can be successfully used as a precursor for alkali-activated materials. Likewise, mineral wastes with low alumina content such as rice husk bark ash (0.4%  $\text{Al}_2\text{O}_3$ ) can also serve to obtain alkali-activated materials.
- Similarly, regarding the silicate content, both spent coffee waste (~1.0%  $\text{SiO}_2$ ) and rice husk bark ash (81.36%  $\text{SiO}_2$ ) can also be used as new precursors in alkali-activated materials.
- Incinerator bottom ash (IBA) shows the most promising future as a novel waste precursor for chemical activation due to its large availability (about  $10^{12}$  tonnes/year), mechanical performance (upward of 32.5 MPa) and versalite range of applications.
- The health hazards and environmental impact of using highly alkali activators is a known issue. Thus, alkali rice husk ash activator (RHAA) could be considered one of the more promising chemical activators recently explored due to its sustainable preparation and potential to be used in the production of sodium waterglass.

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