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A Bibliographic Review of Concrete Obtained by Alkaline Activation and The Specific Case of The Municipal Solid Waste Incineration Slag

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ABSTRACT

The present bibliographic review work focuses on the approach and study of historical processes of slag resulting from the incineration of municipal solid waste, namely: An introduction to the history of Roman civilization and its building habits in the region of Pozzuoli, its engineering and architecture; Alkali-activated ligands, their Zeolitic compositions, geopolymers, chemical reactions and their crystalline phases, amorphous materials and the composition of aluminosilicates; Chemical and structural characterization of alkaline-activated materials and elements; Hybrid cements considered binders containing a percentage of OPC and another percentage of an aluminosilicate precursor and activated alcaline; Origin and treatment of municipal solid waste as well as incineration processes; Hybrid cements containing municipal solid waste incineration slag; An approach to the alkali activation of ligands with slag from municipal solid waste incineration. Finally, a conclusive top-down analysis of these issues.

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Introduction

The first known uses of pozzolans date back to the Roman Empire, when it was discovered that volcanic ash from the region of Pozzuoli, near Vesuvius, when finely ground and mixed with lime, produced a strong and durable mortar. The first explorations started in that region, but were extended to other volcanic areas of Lazio and Campania and later throughout the Mediterranean basin, making use of the different colors of the material, which vary according to their origin. Vitruvius, the Roman engineer and architect who lived in the 1st century BC, had already described four types of pozzolana (black, white, gray, and red) and their uses.

Once their binding properties were discovered, the Romans made extensive use of pozzolans to produce opus caementicium (cementizio), a type of mortar created by mixing pozzolans with lime (typically in a 2:1 ratio) immediately before the addition of water. This mortar is a powerful enough binder to build large structures, such as bridges, domes and long beams, and it has the unique characteristic of setting even when submerged. Extraordinary examples of its use are the dome of the Pantheon in Rome and the jetties of the Roman port of Cosa. The latter were built with pozzolanic mortar apparently placed on the seabed through long tubes that made it possible to fill the molds without mixing it with seawater. The resulting structure was so durable that three of the piers still remain, with their submerged structures in excellent condition, more than 2100 years after their construction.

The use of pozzolanic mortars was abandoned with the fall of the Roman Empire but it was resumed after the European Renaissance and it is at the origin of modern cements. The rediscovery of pozzolans is due to the work of Italian humanists having been promoted by the great Renaissance architects and builders, including Filippo Brunelleschi, who rediscovered the use of quick-setting pozzolanic mortars in the construction of domes and bridges.

The large-scale reintroduction of the use of pozzolans led to the search for alternative sources to natural ones, with multiple non-crystalline silica-rich materials having been found to show the same cementitious properties. Among the artificial pozzolans, calcined clays, fly ash and calcined diatomaceous earth stand out.

Pozzolans are rocks of volcanic origin consisting of a more or less homogeneous mixture of clayey materials, silts and sands, with greater or lesser aggregation, resulting from the alteration by atmospheric agents of volcanic materials rich in non- crystalline silica, especially pumice. Nowadays, the designation of pozzolana has been extended to materials either produced industrially or derived from fly ash or slag from industrial burning processes.

Due to their richness in vitreous silicates, pozzolans are considered acidic sedimentary rocks, with a high content of reactive silica (SiO2), capable of reacting with calcium hydroxide (Ca (OH)2), producing silicates of hydrated calcium (C-S-H), responsible for the mechanical strength of cement. The most common pozzolans are light in color, but depending on the metallic oxides content, their colors may range from whitish to dark gray, including red and pink varieties.

Alkaline-Activated Binders

The research on alkaline-activated cements had a somewhat relevant development- in the former Soviet Union, in the Scandinavian countries and in some countries of Eastern Europe [1].

References point to Glukhovshy as the first researcher who emphasized the differences between the composition of Portland cement, C-S-H and Ca (OH)2, and the basic composition of Earth crust minerals, Zeolitic materials containing alkali metals [2]. Davidovits later developed and patented alkaline activated cements, naming them geopolymers. Based on his investigations, Glukhovshy developed a new type of binder that he called “soil-cement”, with the word “soil” being used because it resembles a natural rock, and “cement” for its binding capacity. They also reported that the polymerization process involves a chemical reaction in a high alkalinity medium, which generates Si-O-Al-O polymeric amorphous bonds, which follow an empirical formula Mn[-(Si-O2)Z-Al-O]n, wH2O- where n is the degree of polymerization, Z is 1, 2 or 3, and M is an alkaline ion, such as sodium or potassium [3,4].

It has also been reported that some geopolymers are similar to amorphous zeolites in which the crystallization stage has not been reached, due to a very rapid reaction during dissolution and condensation, or a very slow reaction when hardening occurs [5]. It was also indicated that most investigations on alkaline- activated binders use inferior products such as blast furnace slag or fly ash, as these materials do not require milling or heat treatment operations, and that other researchers have evaluated the activation possibility of several aluminosilicate minerals [6,7].

Recent articles published by Mehrab Nodehi and Taghvagee on alkaline- activated materials and geopolymers, point to a major obstacle to sustainable development and sustainability in the Construction Materials Industry, due to the high increase of CO2 production, originating from the Common Portland Cement Production Industry, thus highlighted as a relevant emitter of greenhouse gasses, with approximately 8% of the total global annual production of CO2 with reports also pointing to the use of almost 40% of energy production [8,9,10,11].

Torgal and Jalali have also mentioned that ligands obtained by alkaline activation have been receiving increasing attention, either due to the need to reduce greenhouse gas emissions, or due to the need for binders that have a superior durability to that of Portland cement, indicating that reinforced concrete structures built with Portland cement have shown their “Achilles heel” regarding their durability, given that their expected lifespan was 100 years in the 50s, 75 years in the 70s and currently it is only 50 years.

Ligands obtained by alkaline activation are synthesized from aluminosilicate material with highly alkaline solutions and are known to be responsible for a lower emission level than Portland cement, to which it must also be added a high capacity to immobilize heavy metals, granting this type of binder an added value. Thus, for the building materials industry to become environmentally “friendly”, one of the most recent alternatives in this area can be seen in the emergence of alkali-activated materials and geopolymers through which Portland cement can be replaced by supplementary cementitious materials that have binding capacity and are generally recognized as the most promising waste-containing materials added to the mix, replacing cement and acting as binding agents [8].

Historically, cementitious materials were selected and chosen to be used in the construction industry, due to their suitability and often favorable properties. Table 1 presents a historical review.

Table 1: Historical Review of Some Important Events Concerning Cements Obtained + Alkaline Activation and Alkaline Cements Adapted from Roy, Torgal and Jalali, Amer, [6,12].

AUTHORS		DESCRIPTION
Hans Kuhl	1908	Slag cement and process of making the same [13]
Kuhl	1930	Investigated setting behavior of slag in the presence of caustic potash.
Chassevent	1937	Measurement of reactivity of slag using alkalis [14]
Feret	1939	Slags used for cement [15]
Purdon	1940	Investigated clinker-free. Alkali-Slag Combinations [13].
Glukhovsky	1957	Synthesized binder using hydrous and anhydrous aluminosilicates.
Glukhovsky	1959	Basesteric and development of alkaline cements
Glukhovsky	1965	First called “alkaline cements” [16]
Davidovits and Cordi	1979	Term “Geopolymer” [17]
Malinowski	1979	Characterization of millennial aqueducts
Davidovits	1982	Mixture Kaolinite-limestone and dolomite with alkalis [3]
Forss	1983	Cement type F (slag cement of low porosity)
Langton and Roy	1983	Characterization of materials in millennial buildings [18]
Davidovits and Sawyer	1985	Patent of the “Pyrament” cement [19]
Krivenko	1986	Systems R2O - RO - SiO2 - H2O [20]
Malolepszy and Petri	1986	Activation of synthetic slags GGBFS [21]
Malek. et al.	1986	Forms of Slag cement-low level radioactive waste [22]
Davidovits	1987	Comparison of millennial and modern concretes [23]
Kaushal et al.	1988	Adiabatic cured nuclear wastes forms [24]
Deja and Malolepsy	1989	Resistance to chloride attack [25]
Roy and Langton	1989	Analogies of millennial concrete [26]
Majunbar et al.	1989	GGBFS activation - C12A7 [27]
Talling and Brandstetr	1989	Alkaline slag activation (GGBFS) [28]
Roy et al.	1989	Rapid setting alkali-activated cements [29]
Wu et al.	1990	Early Activation of slag cement [30]
Roy et al.	1991	Fast setting of alkali ne activated cements [31]

Roy and Silsbee	1992	Review of alkaline activated cements
Palomo and Glasser	1992	Metakaolin with CBC [32]
Roy and Malek	1993	Slag Cement
Glukhovsky	1994	Millennial, modern and future concretes [33]
Krivenko	1994	Alkaline cements [34]
Wang and Scrivener	1995	Microstructure of alkaline activated slag [35]
Shi (Shi, 1996)	1996	Pore structure and permeability of alkali-activated GGBFS
Fernández and Portas	1997	Kinetic studies of activated slag cements [36]
Katz	1998	Microstructure of activated fly ash [37]
Davidovits	1999	Chemistry of geopolymeric technology [38]
Roy	1999	Opportunities activated cements [6]
Palomo et al.	1999	Activated fly ash cement for future [39]
Gong and Yang	2000	Activated red mud/slag cement [40]
Puertas et al.	2000	Activated fly ash/slag cement [41]
Collins and Sanjayan	2001	Activated slag concrete [42]
Palomo and Palacios	2003	Immobilization of hazardous wastes [43]
Grutzeck et al.	2004	Zeolite formation [44]
Feng et al.	2006	Sialite Technology [45]
Duxson et al.	2007	Geopolymer technology: State of the ar [46]
Hajimohammadi et al	2008	One-part geopolymer mixtures [47]
Provis and Van Deventer	2009	Geopolymers [13]
Ravikumar et al.	2010	Activated concretes containing FA or GGBFS [48]
Puertas et al.	2011	C-A-S-H gel model for activated slag cements [49].
Shi et al.	2011	Hybrid alkali ne cement [50]
Tãnzer et al.	2012	Durability of model for activated slag cements [51]
Lee	2013	Alkali-activated FA/GGBFS concrete cured at room temperature [52]
Prabir and Pradip	2014	Hybrid alkaline cement
Palomo et al.	2014	Hybrid alkaline cement
Yuan et al. (2014)	2014	Shrinkage compensation for alkali-activated slag concrete
Pradip and Prabir	2015	Hybrid alkaline cement
Thomas and Peethamparan	2015	Engineering properties of AAC [53].
Ding et al.	2016	Mechanical properties of AAC:Stat-of-art [54]
Rafeet et al.	2017	Mix proportioning of FA/GGBFS based AAC [55]
Ibrahim et al.	2018	Characterization of ambient cured AAC utilizing nano silica [56]
Koenig et al.	2019	Flexural behavior of steel and macro-PP fiber reinforced AAC [57]
Zhang et al	2020	Fabrication and engineering properties of AAC: A review

Purdon in Belgium, used slag activated alkaline with sodium hydroxide, suggesting that the process was basically developed in two stages: a first in which there would be the release of silica, alumina and calcium hydroxide and a second in which there would be formation of hydrated calcium silicates and aluminates as well as regeneration of the caustic solution [58].

From the results obtained, this researcher concluded that the alkali metal hydroxides act as catalysts, so that, through the leaching of this alkali metal from the hardened binder, in amounts similar to those present in the initial mixture, it was possible to prove this theory. Through the results obtained and documented, they defended the possibility of using such residues, -quite available at the time, to reduce the need for Portland cement and reduce incorporated costs. In addition to that, the researcher Joseph Davidovits investigated, developed and patented the ligands obtained by alkaline activation of kaolin and metakaolin as precursors and fire resistant materials, which he later designated as “geopolymer”.

Geopolymers are polymers because they have the ability to transform, polycondense, take shape and harden quickly at low temperatures [4]. In addition, they are inorganic, hard, stable up to temperatures of 1250 °C and non-flammable, that is, they are geopolymers. In terms of structural ligands, this researcher considers it to be a modern adaptation of processes used by Romans and Egyptians, even going so far as to hypothesize, after studies on the pyramids of Egypt, that those constructions use ligands produced by humans instead of traditional natural stone.

Davidovits also found, from chemical and mineralogical studies, that the blocks are not made of natural limestone, but of a binder made from a mixture of limestone from Giza with NaOH, produced on site by mixing lime, sodium carbonate and water [3]. According to analysis carried out, the natural stones are composed of fossilized sheets arranged parallel to each other, and in sedimentary layers. However, in pyramid blocks, these layers are randomly oriented, as it would happen in a traditional binder. X-Ray studies of samples from the various pyramids indicate that calcite (CaCO3) is the predominant crystalline phase. Furthermore, an amorphous material composed of aluminosilicates and an analcite-type zeolite (Na2.Al2O3.4SiO2.2H2O) was also detected in the microstructure [59].

From these investigations, research in this domain has increased exponentially, with a vast set of investigations focusing on the development of a sustainable binding agent, starting to consider the use and study of the physical properties of alkali activated materials, through the use of a variety of waste-based materials and activators [3]. Several investigators have observed the existence of almost 40% of analcite-type zeolites in the composition of mortars discovered at Jericho in the Jordan River valley and at Tel- Ramad in Syria, dated to 7000 BC [60,61]. Furthermore, Langton and Roy analyzed Roman mortars, having discovered analcite in the composition of these binders [18,26].

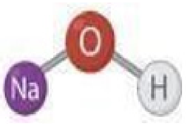
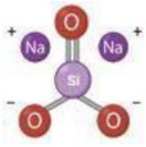
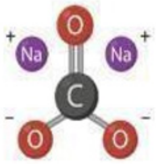
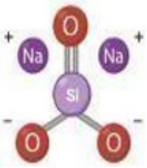
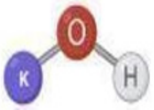
Campbell and Folk showed that the durability of ancient binders was due to the high level of zeolitic and amorphous compounds in their composition [62]. The Belgian researcher Demortier published a more recent study in which very solid arguments are made in defense of - Davidovits' thesis, comparing the resonance spectra for silica and alumina from a sample of the pyramid of Kéops and another from a geopolymeric binder, revealing that the first contains about 15% of geopolymeric binder [63].

Besides that, for Granizo, the presence of zeolites in several ancient cements suggests that they are the stable phase of a long-term conversion, meeting certain hydrothermal conditions, from the initial phases to the formation of zeolitic-type materials [59, 64]. Much of the research on ligands obtained by alkaline activation is related to the activation of blast furnace slag, known as "alkali-slag cement" or "alkali-activated slag cement" (Pacheco and Jalali). Blast furnace slag is a byproduct of the production of iron ore, which has a- substantial amount of calcium in its composition that comes from the calcium carbonate used as a flux (Pacheco and Jalali).

Characterization of Chemical and Structural Elements of Alkali-Activated Materials

Some researchers confirm the existence of two distinct models of alkaline activation: in the first model, the reaction products are of the hydrated calcium silicate type (C-S-H), a good example being the activation of blast furnace slag, a material with a high percentage of oxide and calcium that can be activated with alkaline solutions of low or medium concentration. In the second model, a polymerization reaction is triggered from the material composed essentially of silica and alumina when activated in the presence of highly concentrated alkaline solutions. Table 2 presents the main alkaline activators used by researchers. Additionally, Figure 1 and Figure 2 present the types of poly(sialates) produced and illustrate the alkaline activation processes, respectively.

Table 2: Main Alkaline Activators - Adapted from Duxson [46]

Alkaline Activators	Structure
The sodium hydroxide (NaOH), also known as caustic soda, is an inorganic compound that has a variety of uses in manufacturing including soaps, paper, dyes and petroleum products. As a strong base, it is corrosive in nature and can cause allergic reactions and skin irritations (Miller, 1987). It can be found in liquid and solid states that are colorless and odorless.	
Sodium silicate is a general name for any chemical compound that has sodium oxide, (Na2O) n, and silica, (SiO2) m, in it. It has a variety of applications in the construction industry which include sealing concrete cracks, dissolving agents in alkali-activated materials and an excellent accelerator [65]. Commercially available sodium silicate has a pH of about 10 to 13, inversely related to silica content.	
Sodium carbonate is another inorganic compound that is soluble in water. With the formula Na2CO3, it has a high concentration of bicarbonate that increases the pH or leads to the dissolution of other matters within the medium [66]. This solid material can be produced from natural sources of trona and sodium carbonate brines, as well as the mineral nahcolite (natural sodium bicarbonate sources) which commonly occurs as a decahydrate crystalline that later efflorescence and forms a white powder (Encyclopedia.com) [67,68].	
Sodium metasilicate is the main component of sodium silicate with Formula Na2SiO3. The production of sodium metasilicate is an energy-intensive process that requires the fusion of silica sand (SiO2) with sodium carbonate (sodium carbonate) which occurs at around 1400˚C [69].	
With the KOH formula, **the potassium hydroxide** is a strong base that is marketed in **pallets**, flakes and powder that is known for its corrosive tendency to absorb moisture from the environment. The production of potassium hydroxide is done through the electrolysis of potassium chloride. Serious reactions, skin irritations and other dangerous side effects have been documented as a result of the contact with it [70].	

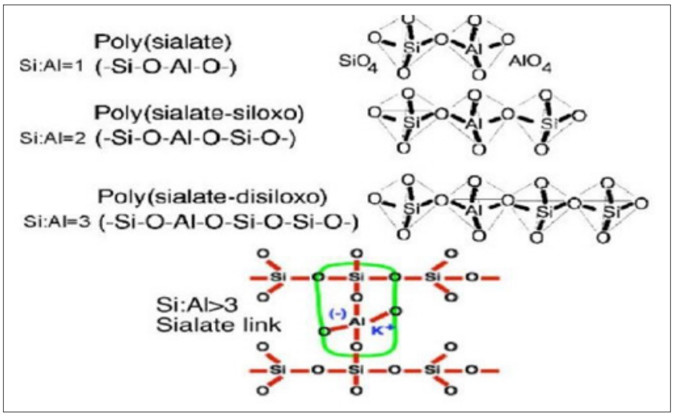


Figure 1: Types of Poly (sialates) - Davidovits [71]

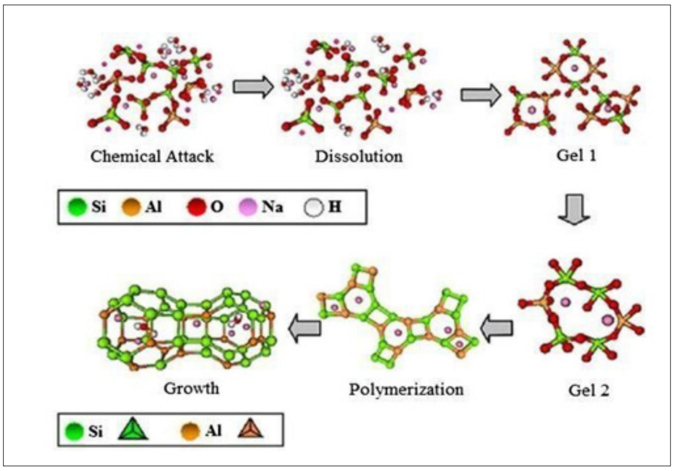


Figure 2: Alkaline Activation Processes - Adapted from Duxson [46]

In the study of some results obtained on the characterization of ligands achieved by alkaline activation (Couto Oliveira n.d.) one sees that it is a hydration reaction of aluminosilicates with alkaline or alkaline-earth substances, namely hydroxides (ROH, R(OH)2), salts of weak acids (R2CO3, R2S, RF), salts of strong acids (Na2SO4, CaSO4.2H2O), or silicate salts of type R2.(n)SiO2, where R is an alkaline ion of type Na, K or Li, or alkaline earth such as Ca [72,73]. At first, the aluminosilicates must undergo a thermal treatment, involving the loss of water and the alteration of the coordination of the aluminum ion with the oxygen [74]. This procedure helps to enhance the results as the material thus shows greater capability of chemically combining.

As an effect of these changes, it can be noticed that the material loses a large part of its crystalline structure, remaining in a practically amorphous state, with high entropy [75]. Thus, aluminosilicates are potential starting materials for alkaline activation, since they have a recognized thermal history. Among them are slags, which can be obtained in blast furnaces, fly ash, obtained by burning coal in thermoelectric power stations, volcanic ash, with natural heat treatment and tile or brick dust, which have been in industrial baking ovens. Obtaining amorphous matrices is reinforced by the cooling phase, as it is normally very fast and critical [72,73,74].

Metakaolin, which can also be activated alkaline, is obtained from kaolins, natural aluminosilicates, resulting from chemical changes in feldspathic rocks (meteorization). For that to happen, it is necessary that the kaolins undergo a heat treatment aiming at dehydroxylation and altering the aforementioned aluminum coordination. It should be noted that kaolins, as well as volcanic ash and certain fly ash, do not belong to the traditional line of mineral binders in which calcium, similarly to what happened with Portland cement, plays a leading role, since they generally have a low or practically zero calcium content [72,73,74].

In the alkaline activation process from kaolinitic precursors (metakaolin) the release of Al and Si elements is observed, while Ca and Si are released from precursors from blast furnace slag [76]. Studies carried out prove that the degree of reaction in the metakaolin solutions activated with sodium silicate (NaSiO4) and sodium hydroxide (NaOH) is greater than if the metakaolin is activated only with NaOH. The fact that the silica present in the sodium silicate reacts faster than the silica in the metakaolin, may serve to prove this conclusion, since a greater proportion of the compound remains unreacted [76].

When studying the alkaline activation of metakaolin using an alkaline solution with sodium silicate, Pinto mentioned an increase in mechanical strength, either in compression, obtaining values from 30 to 60 MPa, or in traction by bending, obtaining values between 5 and 7 MPa [72]. Fernandez-Gimenez and Palomo reported that the use of a solution composed of NaOH and sodium silicate as an alkaline activator, instead of only NaOH, causes an increase of 40-90 MPa only after one day of curing [43,76]. In addition to these, other studies demonstrated that geopolymers produced with metakaolin and activated with NaOH and sodium silicate show an increase in mechanical strength when the Na2O/SiO2 molar ratio decreases [76].

The development of activated alkaline systems based on calcium-rich precursors has been monitored for over a century [8,77]. In this system, precursors such as ground granulated blast furnace slag and Class C fly ash are used in a relatively mild alkaline condition [8,78].

The participation of calcium in this system can be in the form of: (i) Ca (OH)2; (ii) replacing the cations within the mixture and linking it; or, (iii) reacting with dissolved aluminum and silicate species to initially form C-S-H gel [8,79].

This addition of high calcium materials mainly alters the regulation time and the chemistry of the product, where Al3+, Si4+, Ca2+, and Mg2+ are the main network modifiers in the reaction chain [8,80]. These alkaline modifiers result in the formation of calcium aluminum silicate hydrate (C-A-S-H) [8,80,81]. Thus, the higher level of calcium leads to faster hardening of the C-A-S-H gel phase, lower set-up time and higher early strength [8,79,82,83].

This generation process has been reported to increase strength over longer periods of time if followed by curing under ambient conditions, similar to the ordinary Portland cement concrete system that develops hydrated calcium [8,82].

On the opposite side, however, higher drying shrinkage and cracking, higher risk of steel corrosion through chloride ion exchange, and the loss of durability especially at high temperatures (above 300°C) have been reported for high calcium systems [8,84,85].

These adverse effects on the characteristic of alkali-activated materials are reported to be related to the molar ratio of Ca/Si, Al/Si, and the type and amount of activator, as well as the pH level of the medium, and as described by many investigators, the gypsum formation due to the presence of calcium [8,13,77].

Hybrid Alkaline Cements

Recently, a new type of binder, known as hybrid alkaline cement, has been developed [50,86,87]. These materials aim to combine the positive characteristics of ordinary Portland cement with those of alkali- activated materials, with two types of hybrid cements. The first includes the combination of a high proportion of aluminosilicate (above 70%) and Portland cement and the second is a mixture of aluminosilicate with another source of calcium, such as blast furnace slag. These materials are considered mixed Portland cements activated by alkali where the two gels coexist, C-S-H (product of Portland cement hydration) and N- A-S-H (product of alkaline activation of aluminosilicate) [88].

The commercialization of this type of cement is considered highly viable due to its potential inclusion in construction taking into account its environmental, technical and economic advantages. However, the lack of policies, investment and marketing conditions delayed the success of the expansion of this technology. Based on the composition and calcium content of the solid precursor, three types of alkali-activated binder can be defined:

(i) calcium alkali-activated ligands with high calcium content and, (ii) low calcium content and calcium intermediates. According to previous studies, alkali-activated binder with high calcium content are ligands with a Ca/(Si + Al) ratio of about 1, which is commonly a result of an alkaline activation of blast furnace slag [86]. The main reaction product in this group is a calcium aluminosilicate hydrate, or C-A-S-H gel type with a disordered structure similar to tobermorite [85,89].

The low calcium group binders are produced by alkaline activation of low calcium aluminosilicate materials (e.g. metakaolin or class fly ash). The main reaction product in these ligands is a structurally disordered three-dimensional sodium aluminosilicate hydrate (referred to as N-A-S-H or geopolymer) with a zeolite-like structure [85,32,4,90]. These binders generally require heat or steam curing (e.g. at 60°C) to facilitate the dissolution of fly ash or metakaolin and to influence the reactivity of the glass phase in aluminosilicate source materials [46,85].

Bearing in mind that the production of Portland cement currently represents 5% of CO2 emissions worldwide, such a rise in production implies a drastic increase in these emissions, which means a radically opposite stance to that recommended by the Kyoto protocol, which advocates the reduction of emissions in relation to the base year of 1990. And even though energy consumption for clinker production has already reached a level in terms of best practices at 3GJ/ton. According to Torgal and Said, 2008, a limit also seems to have been reached in the clinker/cement ratio. The world's largest cement producer reports having reduced carbon emissions from its cements from 0.767 to 0.685 tons of CO2 per ton of cement from 1990 to 2003 (Lafarge, 2003).

Currently, the cement industry produces cement additives with byproducts of cementitious characteristics, such as slag and fly ash, as a way of reducing both the level of emissions and their cost. (Gielen, 1997) states that cements with fly ash (25% replacement) are responsible for a level of carbon emissions of 0.67 ton of CO2 per ton of cement. Even so, it does not seem clear that this is the way to achieve substantial reductions in carbon emissions generated by the cement industry, and it is more likely that the solution may involve the development of "more environmentally friendly" materials. The present article, according to (Torgal and Jalali), aimed at analyzing the performance of ligands obtained by alkaline activation in terms of their carbon emissions [91]. The issue of carbon emissions from ligands obtained by alkaline activation has been the subject of some controversy. According to Torgal and Jalali, Davidovits was the first author to comment on the low emissions of ligands obtained by alkaline activation of 0.184 ton of CO2 per ton of binder which, when compared to the Portland cement emissions, shows an improvement of 370% [38].

The analysis of the literature on the retraction of alkaline activated binders indicates this as one of the factors that influences the performance of this binder. The phenomenon of shrinkage has been widely studied for Portland cement-based ligands (Torgal and Jalali, 2009). However, it can be accepted that the mechanisms associated with it are, to some extent, similar, although not in the same order of magnitude as those that occur in alkaline-activated ligands.

The shrinkage is due to a phenomenon of volume decrease in part as a result of a decrease in the liquid phase. It is more appropriate to speak of retractions in the plural, because of the various elementary retractions that actually exist: a) Plastic shrinkage, which occurs before adjusting the mixture, by evaporating surface water (Wittmann, 1976; Torgal and Jalali. 2009); b) Shrinkage by drying, which occurs after the end of setting by evaporation of water in the pores (Torgal; Jalali. 2009); c) Autogenous shrinkage, also known as self- drying or chemical drying, defined as volume variation at constant temperature, without exchange of humidity with the outside, and due to the evolution of hydration reactions (Tazawa et al., 1995; Torgal and Jalali. 2009); d) Shrinkage due to temperature variation, similar to the exothermic reaction between water and Portland cement, an exothermic process also occurs in alkaline-activated binders, which will be associated with expansion phenomena that will lead to shrinkage when the temperature drops (Torgal and Jalali).

The importance of shrinkage is generally associated with the decrease in the durability of the material under analysis due to the appearance of cracking and what this represents in terms of the ingress of aggressive substances into the material, and given its ability of resistance to provide a general idea of the quality of the material (Torgal and Jalali). The level of shrinkage is also extremely important, especially if this material can be used, for example, to repair concrete structures. In this case, the existing concrete will prevent this shrinkage, causing the appearance of stresses that can lead to the cracking of the connection zone (Asad, Torgal and Jalali).

The use of low-calcium fly ash allows for a longer setting time and better workability than high-calcium fly ash, which is less available and often has more variable characteristics. Through the use of low calcium fly ash, due to the reduced Ca content, however, the reactivity of the mixture is drastically affected to the point where another precursor with potentially higher calcium content is used or thermal curing becomes the only way to kick-start the chemical reaction [89,39].

Fly ash can be divided into materials with a high calcium content (class C) and low calcium content (class F), which are one of the most commonly used precursors in alkali-activated materials. Low calcium fly ash (class F) has been much more widely exercised as a major precursor in alkali-activated materials because of its availability and potentially better performance [13]. The use of low-calcium fly ash allows a longer setting time and better workability than high-calcium fly ash, which is less available and often has more variable characteristics. Through the use of low calcium fly ash, due to the reduced Ca content, however, the reactivity of the mixture is drastically affected to the point that another precursor with potentially higher calcium content is used or thermal curing becomes the only way to kick-start the chemical reaction [92,93].

Metakaolin results from the hydroxylation of kaolinite Si2O5, Al2(OH)4 that occurs around 750°C. Its main chemical components include silica (SiO2; 44.4-73%) and alumina (Al2O3,~14.5-47.43%), with a variable particle size of 1.20-38 μm and surface area of 2.16-22 m2/g [70,94,95]. Metakaolin is a key component especially used with low calcium alkali-activated materials that adjust the Si/Al of the binder. Metakaolin is reported to increase the polycondensation rate and effectively increase the reactivity of Class F fly ash to form denser nano and microstructures, achieving higher mechanical properties if cured at high temperature [70,96].

In general, silica fume represents a pure silica material; whose use, in an alkali- activated mixture, is usually as charge. In this regard, the literature shows that the use of silica fume due to its small particles has an invariably positive effect on mechanical and durability properties of alkali-activated materials. This trend is aimed at providing more available Si content for further reaction of aluminosilicate sources in the mixture in addition to acting as a filler and reducing the permeability of hardened alkali- activated materials [97,98].

Municipal Solid Waste and Its Incineration

Waste is “any substance or object that the holder discards or intends or is obliged to discard” (Portuguese Decree-Law nº 178/2006, amended and republished by Decree- Law nº 73/2011). The rapid increase in the world population in the last century has generated a rise in municipal solid waste (MSW). Thousands of tons of MSW are produced each day [99]. Municipal solid waste (MSW) has increased exponentially since the rapid world population and consumption habits growth. In 2018, 513kg were generated per capita in Portugal, which corresponds to 5281 million tons. In the EU, 492 kg of municipal waste were generated per capita on average [100].

The incineration of urban solid waste (MSWI) is one of the main management processes of the entities associated with it and has been receiving increasing attention worldwide, hence the fact that many countries address the issue of the beneficial use of this waste, developing plans and strategic management regulations. The rise in MSW production is nowadays largely managed by the incineration method. Typically, this method is implemented through energy recovery in waste-to-energy plants. Basically, waste-to-energy plants burn waste that could not be recovered or recycled. MSW incineration generates energy, which can be transformed into electricity, hot water or steam. The incineration approach reduces MSW volume by about 90% [100].

Municipal solid waste incineration (MSWI) gives rise to two main products, namely fly ash (FA) and bottom ash (BA). The (FA) is collected after the filtration process and carefully sealed to ensure there is no contamination of the local surroundings and then transported to hazardous landfills, treatment plants or salt mines. Since these locations are fully confined, the (FA) cannot leach into the environment [100]. However, significant volumes of fly ash (FA) and especially bottom ash (BA) are still produced by this method, against the unavoidable financial and environmental costs associated with exposure to these byproducts [99].

A common treatment of solid waste produced in urban areas is incineration, with an energy recovery bonus resulting from the caloric content of the waste, which allows the production of electricity, (principle of converting waste to energy (WTE), during the incineration process [99]. This is a very effective procedure due to its ability to reduce waste volumes as well as the associated recovery through energy production [99]. The need for WTE arose from the interconnected phenomena that are happening on our planet, that is, the need for energy and the problem of waste. As the global population continues to grow and living standards increase, dependence on fossil fuels as an energy source is becoming unsustainable as it is causing harmful effects such as exploitation, pollution and greenhouse gas emissions, threatening the sustainability of the planet.

Energy and waste systems policies share mutual concerns about environmental impacts that include greenhouse gas reductions, soil contamination and groundwater contamination. An example of this mutual concern is an energy and climate law introduced by Sweden in 2009, which integrates energy and climate policies as one. The problem of waste is now seen as a response to energy needs [101]. The importance of the WTE is evident when considering the EU's energy policy, which includes two connected goasl for 2020 consisting of a 20% share in renewable energy sources and a 20% reduction in greenhouse gas emissions compared to 1990 levels. It is important to note that WTE is classified as a renewable energy source by the European Directive on Renewable Energy Sources, whose definition of biomass includes the biodegradable part of urban and industrial waste. In addition, these targets should act as steppingstones to further reductions in 2050. For example, the low carbon economy 2050 roadmap emphasizes the importance of electricity, which means the need for non- fossil fuel energy sources such as WTE.

Also, there are two other waste policies that promote WTE. One of them is the Landfill Directive, in which EU Member States have an obligation to reduce the amount of biodegradable municipal waste that goes to landfill. The other is the Waste Framework Directive, which promotes recycling and recovery. WTE is classified as recovery as long as the process meets certain levels of efficiency [101]. Although the volumes of bottom ashes (BA) and fly ashes (FA) are much lower than the total waste, representing a weight reduction of around 80%, their recycling by integration in any industrial process is an attractive possibility [50,99].

The WTE meets the two main objectives of waste management (Brunner & Rechberger). First, the protection of humans and the environment, such as emissions from incineration that are so technologically advanced that the compounds released into the air, water or soil are not threatening to humans or the environment. The second objective is the conservation of resources and the recovery of materials, which WTE processes by nature positively affect, since in WTE plants, urban solid waste contributes to energy recovery and suffers a reduction in its volume by 90% and its weight by 60%.

It is a process widely applied in several countries, but with emphasis in Europe where, according to information provided by the European Confederation of Waste and Energy (CEWEP), 492 WTE plants operate and contributed to the incineration of 70 MT, in 2017, with bottom ash being the main byproduct obtained during waste treatment, and classified as hazardous waste (EWC 19 01 11) or non-hazardous waste (EWC 19 01 12), depending on the concentration or not of hazardous substances. In the recent past, one of the concerns with MSWI was atmospheric pollution by dioxin ($C_4H_4O_2$), furan (C_4H_4O) and heavy metals originating from MSW. Subsequently, emissions were drastically reduced through the implementation of APC devices to treat gases of a toxic nature using dry, semi-dry and wet scrubbing mechanisms. Later, the use of APC devices shifted the concern from air pollution to leachate from ash disposal in landfills, and RDF processes were reported to provide significant control over heavy metal release, reducing Pb to 52%, Cd to 73% and Cr to 63%.

In general, bottom ash is composed of Si, Al, Ca and Na oxides, and a small amount of heavy metals. And they undergo prior stabilization through an outdoor maturation treatment of 2–3 months, consisting of their carbonation and pH stabilization at values between 8–10 [102].

Although BA is significantly less polluting than FA, it still has a considerable content of heavy metals [99]. In addition, there are several methods, already disclosed and commonly applied, to deal with MSW fly ash, namely the treatment and landfilling as a hazard, solidification and removal of heavy metals [99,103].

The byproduct resulting from the maturation treatment is a bottom ash that is valued for engineering purposes. The main fields of application of BA as a secondary material are civil engineering, chemical engineering and the construction sector [104]. Although the municipal solid waste incineration rate (MSWI) varies significantly from country to country and, more importantly, between different areas of the globe, it can reach 50-58% in some parts of Northern European countries [99]. According to EUROSTAT data, the incineration approach has been increasing in European countries. In 2017, European waste-to-energy plants treated around 96 million tonnes of MSW and around 19 million tonnes of MIBA were generated (CEWEP) [105]. Several EU countries use MIBA as an alternative to non- renewable natural resources such as gravel and sand [100]. However, new applications of BA have emerged in recent years for their use as a precursor in cements obtained by alkaline activation due to their composition rich in silicates and aluminosilicates, making them an alternative to ordinary Portland cement [50,100,106].

Hybrid Cement with MSWIS

According Lurdes Lopes in his approach on the production of a cementitious material based on MSWIS, pretreatment, such as grinding, is necessary, as shown in figure 3 - a fact also addressed by different authors [107]. One article (Jiaqi Li) shows a critical overview of the pretreatment method that optimizes the use of MSWIS ash in cement/concrete and the influences of MSWIS ash on cement/concrete performance. Recent studies suggest that MSWIS ash can be used to produce concrete, bricks and other building materials with or without pretreatment of ash MSWIS [108,109]. Many pretreatment methods have been applied to lower the content of chlorides, HMs, and or organic matters of MSWI ash (Jiaqi Li). The industrial pretreatment methods include water-washing, aging, magnetic separation, mechanical separations, and eddy current separation. The separation methods reclaim ferrous and non-ferrous metals (including precious metals, aluminum, and HMs [110]. These industrial- scale separation technologies are mature and very commonly used (Jiaqi Li).

Figure 3: Working process of a ball mill usually used in the first stages of a laboratory analysis, as a pretreatment process of physical nature, consisting of the fragmentation of slags for the purpose of reducing the particle diameter [107].

Water-washing is the most common industrial method to remove soluble salts, such as, NaCl, KCl,or $CaCl_2$. From MSWI ash, more specifically FA (Jiaqi Li). This pretreatment is cost-efficient to remove chlorides, which trigger the corrosion of steel rebar and concrete mixers. However, water-washing typically can lower the chloride content down to 0,5 wt.% due to the presence of low-solubility chlorides [111]. Calcium oxychloride (CaOCl) is challenging to remove by only one time of washing. Mao et al. found that the influence of water-to-solid ratios on chlorides removal was less pronounced when the ratio was over three, and the replication of washing at this ratio was more efficient and water-saving than at a ratio of 20 [112]. Because water-washing is essentially a leaching process at high water-to-solid ratios, it yields leachates with HMs, reducing the HMs content of washed MSWI ash [113].

After appropriate treatments, MSWI ash, as a pozzolamic material, can potentially lessen the global shortage of SCMs. MSWI ash must be appropriately managed as SCMs in academic studies and practical applications. For example, MSWI ash must not be used to replace low-grade PC [103]. Thus, such MSWI ash incorporated cement-based materials are considered products of the stabilization/solidification (S/S) process. These low- value products are more suitable as landfills with low toxic leachability or construction materials in niche markets [114]. Thus, the influence of unwashed ash on cement settings is complex; prolonged and shortened setting time of raw ash-containing pastes have been reported. In addition, soluble Cl triggers steel-rebar corrosion [115,116]. The metallic Al and Zn in raw ash cause the expansion and cracking of low-strength ash-containing pastes [117].

The low amorphous content and large grain size of BA may limit its reactivity in PC systems. Thus, raw ash contributes little to strength development. Even with the addition of alkaline activators ($CaSO_4$ and Na_2SO_4), the compressive strength of hybrid cement with 40% MSWI mix ash is still~40% lower than OPC [118]. The low strength of blended cement incorporated with raw MSWI ash limits its wide use as standard-performance construction material despite its HMs immobilization advantage. These low-strength blended cement-based materials from the SS process are niche products [114]. Thus, pretreatment of MSWI ash is suggested for its appropriate utilization as SCMs. The possible use of treated MSWI BA as SCMs depends on many factors, e.g., amorphous content, particle size, and compositions of PC and treated BA. Raw BA particle sizes are large; thus, milling and sieving are common processes. Jure et al. partially replaced OPC with milled BA, and the compressive strengths at 3-28 days were comparable to the 42.5R OPC group when the cement substitution was ‹ 20 wt.%. A 10% compressive strength reduction was observed at a substitution level of 30% at 28 days.

The leachability of the BA incorporated group met regulatory limits [119]. Similarly, Zhang and Zhao replaced 30 wt.% 42.5R OPC with wet-milled BA, while the blended group only exhibited similar or lower strengths compared to the pure OPC counterpart from 1 to 90 days [120]. Bertolini et al. compared the influences of wet and dry- milling of BA on the mechanical properties of concrete [121]. Concrete containing cement substituted with 30 wt.% wet-milled BA exhibited similar or higher compressive strengths compared to 52.5R OPC concrete from 1 day to 180 days, while concrete containing 30 wt.% dry-milled BA substitution exhibited 55% lower strength. The strength difference may be explained by the finer grains of wet-milled BA compared to dry-milled BA and the consumption of metallic Al and Zn. The incorporation of unwashed or other washed FA in mortars diminished compressive strength [122]. Higher cement replacement levels, e.g., 30 wt.%, also resulted in lower strengths, according to Bertolini et al. [121].

Alkali-Activated Binders with MSWI

In the field of use of municipal solid waste incineration slags, such as alkaline activation binders, its application is recorded in 1930 (Investigated setting behavior of slags in the presence of caustic potash); by the German Engineer and Chemist Kuhl in 1937 (Measured reactivity of slag using caustic potash and soda solution); by Chassevent in 1940 (Investigated clinker-free cements consisting of slag and caustic soda or slag and caustic alkalis produced by a base and an alkaline salt); by Purdon in 1957 (Synthesized binder using hydrous and anhydrous aluminosilicates-glassy rocks, clays, metallurgical slags, etc. and alkalis, proposed Me_2O-MeO-Me_2O 3-SiO 2-H_2). The cementing system, called "soil cement" binder by Russian Glukhovsky (Shi; Krivenko; Della Roy) [123]. We can mention that, for slag, the development of alkaline-activated ligands made a significant contribution in 1940 with Purdon's study of blast oven slag activated with sodium hydroxide, having observed that hydroxides played a role as catalysts (Torgal, Castro-Gomes and Jalali). Years later, in 1957, Glukhovsky developed a study dedicated to the discovery of a new ligand based on low or no calcium aluminosilicate materials, naming it "cement soil" (Pacheco- Torgal, Shi; Krivenko; Della Roy).

Although there was an increase in scientific production on alkaline activation in the decades following 1990, it was only in the 21st century that new publications on the case appeared, increasingly with some approach on other slags, but with little approach to slags from the incineration of municipal solid waste MSWIS. One of the factors that some bibliography addresses about the weak insertion of MSWIS in current studies is - that alkaline- activated ligands are divided into three categories [78]. A) Materials with high calcium content (CaO-SiO_2-Al_2O_3), B) Materials with low calcium content (SiO_2-Al_2O_3) and C) Materials with intermediate calcium content. The most used material in category A is blast oven slag ($SiO_2+CaO \geq 70\%$), having as main reaction products calcium silicates hydrated with aluminum in its composition (C-A-S-H), followed by a series of secondary products that depend on the nature of the precursor, the activator and its concentration, in addition to the healing conditions and Ph [78,85]. And category B shows materials that are rich in silicon and aluminum and have a low calcium, such as some fly ash and metakaolin [123].

X-Ray diffractogram of the fly ash, in which it is verified that the fly ash presents different peaks of diffraction of crystalline phases, which, according to Provis et al. and Williams et al. are phases that arise during the burning of mineral coal at very high temperatures (1200 -1600ºC) and in a highly oxidizing environment [13,81]. Diffraction peaks are identified correspondents to crystalline phases of Quartz (SiO_2), Mulita ($Al_6Si_2O_3$) and Hematite (Fe_2O_3) (Azevedo et al.,). The diffractogram also presents a period between 10 and 40º (2Θ), which indicates the presence of amorphous material, where in the vast majority, amorphous (reactive) amorphous aluminosilicates will react during ash activation with alkaline solutions [124].

X-ray diphratogram of metacaulim, where it is observed that the metacaulin presents a high crystallin, due to the presence of Quartz (SiO2), Anatásio (TiO_2), Ilita {$(K,H_3O)(Al,Mg,Fe)2(Si,Al)4O10[(OH)2, (H_2O)]$} and Kaolinite [$Al_2Si_2O5(OH)4$] (MAURI 2009).

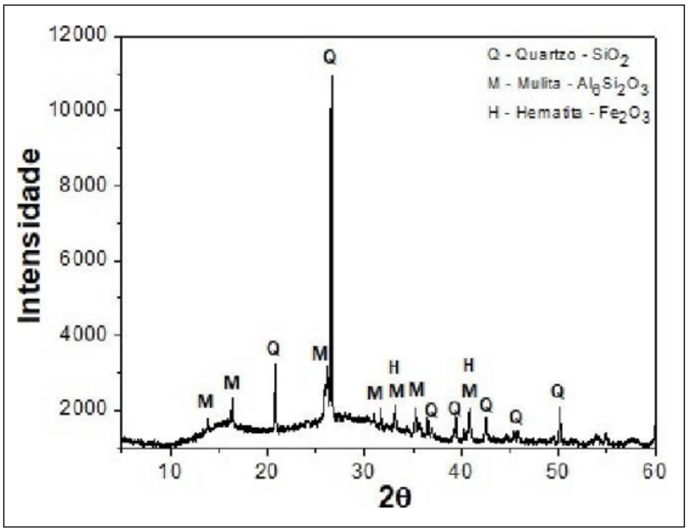


Figure 4: X-Ray Diffractogram of the Fly Ash

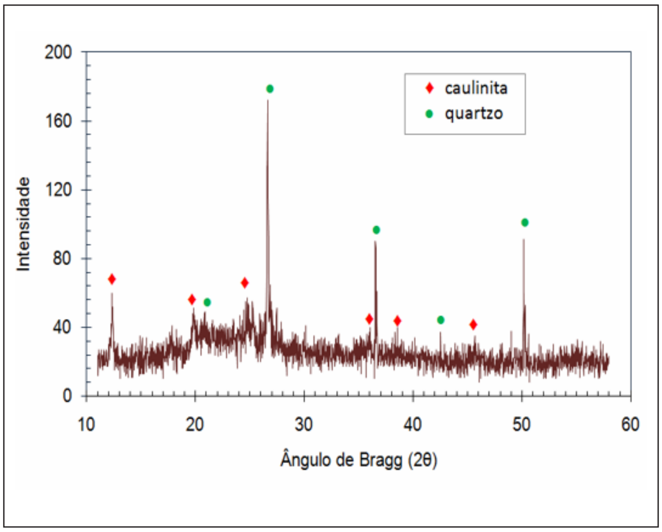


Figure 5: X-Ray Diffractogram of Metakaolin

In category C, the system type is hybrid in nature with combinations of agglomerates rich in allots and other reactive sources of calcium. This category allows the use and consequent recovery of residues and byproducts previously considered as little reactive, however, when combined with other materials they can generate good indicators as results [123]. Its main reaction products are found in the combination of gels generated by systems with low and high calcium content, N-A-S-H and C-A-S-H, and in solutions with high pH, the solubility of calcium decreases and the Na+ ion can replace some Ca2+ ions in the formation of products, generating gels of type (N,C)-A-S-H. [85,123].

Final Remarks

From the present research, the relevant remarks are drawn:
In the activation of slag with silicate and sodium hydroxide, the setting time depends on the activator composition. Researchers have observed initial and final setting times of 2 and 8 minutes, for an activator with 8% Na_2O and Ms=1.25.

In slag activated with sodium silicate, researchers report very variable setting times, 2.75 to 4.25 hours for the beginning of setting and between 3.25 and 5.5 hours for the end of setting.

In slag activated with silicate and sodium hydroxide, researchers have observed a correlation between porosity and compressive strength, however, it states that only 70 to 80% of the variation in mechanical strength can be explained by the variation in pore volume, with the remainder due to chemical composition.

In slag activated with sodium hydroxide and carbonate and Portland cement binders, researchers have observed a much lower porosity than that of Portland cement.

In slag slurries activated alkaline with sodium hydroxide and sodium silicate with A/L=0.5, researchers obtained relatively low and increasing strengths of 8, 16 and 39 MPa respectively at 1, 7 and 28 days, however when using slag mortars (aggregate/gray=2) the strength made faster progress in the first days, with numbers at 9, 21 and 26 MPa.

In a study with concretes based on alkaline activated slag, with sodium hydroxide and sodium silicate and with A/L ratio=0.5, researchers obtained compressive strengths of 16 MPa, 36 and 46 MPa respectively after 1, 7 and 28 days and 6.5 MPa at the 28 day curvature.

In mortars with slag (aggregate/slag=2) and with an A/L ratio=0.51 activated with sodium silicate and sodium hydroxide, strengths of about 100 MPa in compression and 11 MPa in bending were obtained.

The pretreatment of MSWIS has shown that its application reduces the content of chlorides, heavy materials and some organic material issues, and that washing with water is a common method for removing soluble salts such as NaC_1, KC_1 or CaC_{12}.

Wet grinding provides a basic environment for the dissolution of al-metallic aluminum in slag, and some comparative studies between the use of wet and dry grinding materials have shown that there is a greater performance in the compressive forces of mixtures containing wet grinding materials [125-132].

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References

1. Torgal FM, Alves SP, Castro Gomes JP, Jalali S (2007) Alkali-Activated Tungsten Mine Waste Mud Binder versus OPC Concrete. Acid and Abrasion Resistence. Alkali Activated Materials-Research, Production and Utilization 3rd Conference 693-700.
2. Glukhovsky VD (1959) Soil silicates, in Russian. Kiev, Gosstroyizdat 154.
3. Davidovits J (1982) Mineral Polymers and Methods of Making Them. US Patent 4349386.
4. Davidovits J (1991) Geopolymers: Inorganic Polymeric New Material. J. Thermal Analysis 37: 1633-1656.
5. Fernández-Jiménez A, Palomo A (2005) Composition and Microstructure of Alkali Activated Fly Ash Binder. Cement and Concrete Research 35: 1984-1992.
6. Roy DM (1999) Alkali-activated cements Opportunities and challenges. Cement and Concrete Research 29: 249-254.
7. Xu Hua, Deventer JSJ (2000) The geopolymerisation of alumino-silicate minerals. International Journal of Mineral Processing 59: 247-266.
8. Mehrab N, Taghvaee VM (2021) Circular Economy and Sustainability-Binder Alkali Activator. Ingram School of Engineering. San Marcos: Texas State University.
9. Arrigoni A, Panesar DK, Duhamel M, Opher T, Saxe S (2020) Life cycle greenhouse gas emissions of concrete containing supplementary cementitious materials: cut-off vs. Substitution. Journal of Cleaner Production 263: 121465.
10. Lehne J, Preston F (2018) Chatham House Report Making Concrete Change Innovation in Low-Carbon Cement and Concrete. The Royal Institute of International Affairs https://www.chathamhouse.org/2018/06/making-concrete-change-innovation-low-carbon-cement-and-concrete.
11. Zhao X, Hwang BG, Lim J (2020) Job Satisfaction of Project Managers in Green Construction Projects: Constituents, Barriers, and Improvement Strategies. Journal of Cleaner Production 246: 118968.
12. Amer I, Mohamed K, El-Feky MS, Ahmed R, Mohamed AK (2021) A review on alkali-activated slag concrete. Ain Shams Engineering Journal 12: 1475-1499.
13. Provis JL, Van Deventer JSJ (2009) Geopolymers: structures, processing, properties and industrial applications. Elsevier https://www.sciencedirect.com/book/9781845694494/geopolymers.
14. Chassevent L (1937) Hydraulicity of Slags. Compt Rend 205: 670-672.
15. Feret R (1939) Slags for the Manufacture of Cement. Rev Mater Constr 1-145.
16. Glukhovsky VD (1965) Soil Silicates: their properties, technology and manufacturing and fields of application. DTech. Sc. Thesis, Kiev, Civ. Eng. Institute.
17. Davidovits J, Cordi SA (1979) Synthesis of New High Temperature Geo-Polymers for Reinforced Plastics/Composites. PACTEC '79 Society of Plastics Engineers at Costa Mesa, California, USA 151-154.
18. Langton CA, Roy DM (1983) Longevity of Borehole and Shaft Sealing Materials: Characterization of Ancient Cement-Based Building Materials. MRS Online Proceedings Library 26: 543-549.
19. Davidovits J, Sawyer JL (1985) Early High-Strength Mineral Polymer. Google Patents https://patents.google.com/patent/US4509985A/en.
20. Krivenko PV (1986) Synthesis of Binders with Required Properties in the System R2ORO-R2O3- SiO2- H2O. Doct. Tech. Sc. Degree Thesis. Polytech. Institute, Kiev, Ukraine.
21. Malolepszy J (1986) Activation of Synthetic Melilite Slags by Alkalies. In: Proceedings of the 8th International Congress on the Chemistry of Cement. Rio de Janeiro Brazil 4: 104-107.
22. Malek RIA, Roy DM, Barnes MW, Langton CA (1985) Slag Cement-Low Level Radioactive Waste Forms at Savannah River Plant. American Ceramic Society annual meeting, Cincinnati, OH, USA https://www.osti.gov/biblio/5807992.
23. Davidovits J (1988) Ancient and Modern Concretes: What Is the Real Difference? Geopolymer 1: 93-106.
24. Kaushal S, Roy DM, Licastro PH (1988) Heat of hydration and characterization of reaction products of adiabatically

cured fly ash and slag mixtures. MRS Online Proceedings Library 136: 87-97.

25. Deja J, Malolepszy J (1989) Resistance of Alkali-Activated Slag Mortars to Chloride Solution. Spec Publ 114: 1547-1564.
26. Roy DM, Langton CA (1989) Studies of Ancient Concretes as Analogs of Cementitious Sealing Materials for Repository in Tuff. L.A-11527-MS Los Alamos Nacional Laboratory https://www.osti.gov/biblio/60684.
27. Majumbar AJ, Singh B, Edmonds RN (1989) Hydration of mixtures of C12A7 and granulated blastfurnace slag. Cement and Concrete Research 19: 848-856.
28. Talling B, Brandstetr Talling J, Bob Lars Olof, Jiří Brandštetr (1989) Present State and Future of Alkali-Activated Slag Concretes. SP-114: Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete: Proceedings of the Third International Conference.
29. Roy DM, Silsbee MR, Wolfe-Confer D (1989) New Rapid Setting Alkali Activated Cement Compositions. MRS Online Proc Libr Arch 179: 179-203
30. Wu X, Jiang W, Roy DM (1990) Early activation and properties of slag cement. Cement and Concrete Research 20: 961-974.
31. Roy DM, Silsbee MR (1991) Alkali Activated Cementitious Materials: An Overview. MRS Online Proc Libr Arch 245: 153-164.
32. Palomo A, Glasser FP (1992) Chemically-bonded cementitious materials based on metakaolin. British ceramic. Transactions and journal 91: 107-112.
33. Glukhovsky VD (1994) Ancient, Modern and Future Concretes. In: Proceedings of the First International Conference on Alkaline Cements and Concretes 1-9.
34. Krivenko PV (1994) Alkaline Cements. Proceedings of the 1st International Conference on Alkaline Cements and Concretes, Kiev. Ukraine 1: 11-129.
35. Wang SD, Scrivener KL (1995) Hydration products of alkali activated slag cement. Cement and Concrete Research 25: 561-571.
36. Fernández-Jiménez A, Puertas F (1997) Alkali-activated slag cements: Kinetic studies. Cement and Concrete Research 27: 359-368.
37. Katz A (1998) Microscopic Study of Alkali-Activated Fly Ash. Cement and Concrete Research 28: 197-208.
38. Davidovits J (1999) Chemistry of Geopolymeric Systems Terminology. Proceedings of Geopolymer. International Conference on Geopolymer France 9-39.
39. Palomo A, Grutzeck MW, Blanco MT (1999) Alkali-activated fly ashes: A cement for the future. Cement and Concrete Research 29: 1323-1329.
40. Gong C, Yang N (2000) Effect of Phosphate on the Hydration of Alkali-Activated Red Mud- Slag Cememtitious Material. Cement and Concrete Research 30: 1013-1016.
41. Puertas F, Martinez-Ramirez S, Alonso S, Vazquez T (2000) Alkali-activated fly ash/slag cements: Strength behaviour and hydration products. Cement and Concrete Research 30: 1625-1632.
42. Collins F, Sanjayan JG (2001) Microcracking and strength development of alkali activated slag concrete. Cement and Concrete Composites 23: 345-352.
43. Fernandez-Jiménez A, Palomo A (2003) Characterisation of fly ashes. Potential reactivity as alkaline cements. Fuel 82: 2259-2265.
44. Grutzek M, Kwan S, DiCola M (2004) Zeolite formation in alkali-activated cementitious systems. Cement and Concrete Research 34: 949-955.
45. Feng XP, Sun HH, Liu XM (2006) Sialite Technology. Advanced Materials Research 11-12: 615-618.
46. Duxson P, Jiménez AF, Provis J, Lukey GC, Palomo A, et al. (2007) Geopolymer Technology: The Current State of the Art. Journal of Materials Science 42: 2917-2933.
47. Hajimohammadi A, Provis JL, Van Deventer JSJ (2008) One-Part Geopolymer Mixes from Geothermal Silica and Sodium Aluminate. Ind Eng Chem Res 47: 9396-9405.
48. Ravikumar D, Peethmparan S, Neithalath N (2010) Structure and strength of NaOH activated concretes containing fly ash or GGBFS as the sole binder, Cement and Concrete Composites 32: 399-410.
49. Puertas F, Palacios M, Manzano H, Dolado JS, Rico A, et al. (2011) A model for the C-A-S-H gel formed in alkali-activated slag cements. Journal of the European Ceramic Society 31: 2043-2056.
50. Wei Y, Shimaoka T, Saffarzadeh A, Takahashi F (2011) Mineralogical characterization of municipal solid waste incineration bottom ash with an emphasis on heavy metal-bearing phases. Journal of Hazardous Materials 187: 534-543.
51. Tänzer R, Ehrenberg A, Stephan Dietmar (2012) Concrete based on alkali-activated granulated blast-furnace slag (Part 1). Betonwerk und Fertigteil-Technik/ConcretePlant and Precast Technology 78: 25-33.
52. Lee NK, Lee HK (2013) Setting and mechanical properties of alkali-activated fly ash/slag concrete manufactured at room temperature. Construction and Building Materials 47: 1201-1209.
53. Thomas RJ, Peethamparan S (2015) Alkali-activated concrete: Engineering properties and stress–strain behavior. Construction and Building Materials 93: 49-56.
54. Ding Y, Dai JG, Shi CJ (2016) Mechanical properties of alkali-activated concrete: A state- of-the-art review. Construction and Building Materials 127: 68-79.
55. Rafeet A, Vinai R, Soutsos M, Sha W (2017) Guidelines for mix proportioning of fly ash/GGBS based alkali activated concretes. Construction and Building Materials 147: 130-142.
56. Ibrahim M, Johari MAM, Rahman MK, Maslehuddin M, Mohamed HD (2018) Enhancing the engineering properties and microstructure of room temperature cured alkali activated natural pozzolan based concrete utilizing nanosilica. Construction and Building Materials 189: 352-365
57. Koenig A, Wuestemann A, Gatti F, Rossi L, Fuchs F, et al. (2019) Flexural behaviour of steel and macro-PP fibre reinforced concretes based on alkali-activated binders. Construction and Building Materials 211: 583-593.
58. Purdon AO (1940) The action of alkaline on alkaline-furnace slag. J Soc Chem Ind.
59. Torgal FP, Castro Gomes JD, Said J (2007) Binders obtained by alkaline activation of residual sludge from the Panasqueira mines. Polytechnic Institute of Castelo Branco, University of Beira Interior, University of Minho https://www.researchgate.net/publication/277109331_Ligantes_obtidos_por_activacao_alcalina_de_lamas_residuais_das_Minas_da_Panasqueira_parte_II_durabilidade_e_comportamento_ambiental.
60. Contenson Hde, Courtois LA (1979) About Lime Vases. Research on Their Manufacture and Origin. Paleorient 5: 177-182.
61. Perinet G, Contenson H, Courtois L (1980) Etude Mineralogique de Vaisselles Blanches de Ras-Shamra et Tell Ramad (Syrie). Compte Rendu Acad. Sci. 143-144.
62. Campbell DH, Folk Robert L (1991) The Ancient Egyptian Pyramids-Concrete or Rock. Concrete International 13: 29-44.
63. Demortier G (2004) PIXE, PIGE and NMR study of the

masonry of the pyramid of Cheops at Giza. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 226: 98-109.

64. Granizo ML (1998) Alkaline Activation of Metakaolin: Development of New Cementitious Materials. Doctoral Thesis, Autonomous University of Madrid https://repositorio.uam.es/handle/10486/667803?locale-attribute=es.
65. Hocking MB (1985) Industrial Bases by Chemical Routes. In: Modern Chemical Technology and Emission Control. Springer, Berlin, Heidelberg 122-133.
66. Speight JG (2017) Industrial Inorganic Chemistry, in Environmental Inorganic Chemistry for Engineers. Butterworth-Heinemann https://www.perlego.com/book/1833005/environmental-inorganic-chemistry-for-engineers-pdf.
67. Haneke KE (2002) Sodium Metasilicate Pentahydrate and Sodium Metasilicate Nonahydrate. Review of Toxicological Literature https://ntp.niehs.nih.gov/sites/default/files/ntp/htdocs/chem_background/exsumpdf/sodiummetasilicate_508.pdf.
68. Potassium Hydroxide-Encyclopedia. Encyclopedia.com https://www.encyclopedia.com/science/academic-and-educational-journals/potassium-hydroxide.
69. Kubba Z, Huseien GF, Mohd Sam AR, Shah KW, Asaad MA, et. al. (2018) Impact of curing temperatures and alkaline activators on compressive strength and porosity of ternary blended geopolymer mortars. Case Studies in Construction Materials 9: e00205.
70. Torres-Carrasco M, Reinosa JJ, de la Rubia MA, Reyes E, Peralta Alonso F, Fernández JF (2019) Critical aspects in the handling of reactive silica in cementitious materials: Effectiveness of rice husk ash vs nano-silica in mortar dosage. Construction and Building Materials 223: 360-367.
71. Davidovits J (2005) Geopolymer chemistry and sustainable development. Proceedings of the World Congress Geopolymer 9-15.
72. Pinto AT (2004) Binding systems obtained by alkaline activation of metakaolin. Minho's university. PhD final thesis https://www.researchgate.net/publication/277047810_Sistemas_ligantes_obtidos_por_activacao_alcalina_do_metacaulino
73. Pinto AT (2006) Introduction to the Study of Geopolymers. Publisher UTAD, Portugal 105: 2006.
74. Oliveira MJJC (2014) Characterization of the mechanical behavior of binder systems obtained by alkaline activation; time course and activator composition. Faculty of Science and Technology at the University of Combra https://estudogeral.uc.pt/handle/10316/38451.
75. Chang R, Goldsby Kenneth (1994) Chemical. Lisbon: Ed. McGraw-Hill.
76. Severo C (2013) Particular characteristics and scientific principles of alkaline- activated materials. Electronic Magazine of Materials and Processes 8: 55-67.
77. Provis JL, Bernal SA (2014) Binder Chemistry-Blended Systems and Intermediate Ca Content. RILEM State-of-the-Art Rep 13: 125-144.
78. García-Lodeiro I, Palomo A, Fernández-Jiménez A (2015) An overview of the chemistry of alkali-activated cement-based binders. Woodhead Publishing 19-47.
79. Guo X, Shi H, Chen L, Dick WA (2010) Alkali-activated complex binders from class C fly ash and Ca-containing admixtures. Journal of Hazardous Materials 173: 480-486.
80. Shi C, Qu B, Provis JL (2019) Recent progress in low-carbon binders. Cement and Concrete Research 122: 227-250.
81. Temuujin J, Williams RP, van Riessen A (2009) Effect of mechanical activation of fly ash on the properties of geopolymer cured at ambient temperature. Journal of Materials Processing Technology 209: 5276-5280.
82. Topark-Ngarm P, Chindaprasirt P, Sata V (2014) Setting Time, Strength, and Bond of High-Calcium Fly Ash Geopolymer Concrete. Journal of Materials in Civil Engineering 27: 04014198.
83. Puligila S, Mondal P (2013) Role of slag in microstructural development and hardening of fly ash-slag geopolymer. Cement and Concrete Research 43: 70-80.
84. Collins F, Sanjayan JG (2000) Cracking tendency of alkali-activated slag concrete subjected to restrained shrinkage. Cement and Concrete Research 30: 791-798.
85. Sufian Badar M, Kupwade-Patil K, Bernal SA, Provis JL, Allouche EN (2014) Corrosion of steel bars induced by accelerated carbonation in low and high calcium fly ash geopolymer concretes. Construction and Building Materials 61: 79-89.
86. Nath P, Sarker PK (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: 205-214.
87. Garcia-Lodeiro I, Fernandez-Jimenez A, Palomo A (2013) Hydration kinetics in hybrid binders: Early reaction stages. Cement and Concrete Composites 39: 82-92.
88. Palomo A, Maltseva Olga, García-Lodeiro I, Fernández-Jiménez A (2013) Hybrid alkaline cements. Part II: The clinker factor. Romanian Journal of Materials 43: 74-80.
89. Thomas R, Ye H, Radlińska A, Peethamparan S (2016) Alkali-Activated Slag Cement Concrete: A closer look at a sustainable alternative to portland cement. Concrete International 38: 33-38.
90. Palomo A, Alonso S, Fernandez-Jimenez A, Sobrados I, Sanz J (2004) Alkaline Activation of Fly Ashes. A NMR Study of the Reaction Products. Journal of American Ceramic Society 87: 1141-1145.
91. Torgal FP, Said J (2015) Binders Obtained by Alkaline Activation. Part 2- Environmental Benefits. University of Minho, Department of Civil Engineering-Guimarães, Portugal.
92. Shekhovtsova J, Zhernovsky I, Kovtun M, Kozhukhova N, Zhernovskaya I, et al. (2018) Estimation of fly ash reactivity for use in alkali-activated cements - A step towards sustainable building material and waste utilization. Journal of Cleaner Production 178: 22-33.
93. Abdel-Gawwad HA, García SRV, Hassan HS (2018) Thermal activation of air cooled slag to create one-part alkali activated cement. Ceramics International 44: 14935-14939.
94. Rakhimova NR, Rakhmov RZ (2019) Reaction products, structure and properties of alkali- activated metakaolin cements incorporated with supplementary materials – a review. Journal of Materials Research and Technology 8: 1522-1531.
95. Idir R, Cyr M, Pavoine A (2020) Investigations on the durability of alkali-activated recycled glass. Construction and Building Materials 236: 117477.
96. Winnefeld F, Leemann A, Lucuk M, Svoboda P, et al. (2010) Assessment of phase formation in alkali activated low and high calcium fly ashes in building materials. Construction and Building Materials 24: 1086-1093.
97. Luukkonen T, Abdollahnejad Z, Yliniemi J, Kinnunen P, Illikainen M (2018) Comparison of alkali and silica sources in one-part alkali-activated blast furnace slag mortar. Journal of Cleaner Production 187: 171-179.
98. Sun S, Lin J, Zhang P, Fang L, Ma R, et al. (2018)

Geopolymer synthetized from sludge residue pretreated by the wet alkalinizing method: Compressive strength and immobilization efficiency of heavy metal. Construction and Building Materials 170: 619-626.

99. Cristelo N, Segadães L, Coelho J, Benedita Chaves, Nadine RS, et al. (2020) Recycling municipal solid waste incineration slag and fly ash as precursors in low-range alkaline cements. Waste Management 104: 60-73.
100. Ana Mafalda M, Sousa-Coutinho J (2022) Incineration of urban solid waste and recycling of ash into concrete: preliminary approach with port waste. Construction and Building Materials-Elsevier.
101. Guziana B, Song H, Daianova L, Thorin E, Yan J, et al. (2011) Scenarios for waste-to-energy use-swedish perspective. Researchgate https://www.researchgate.net/publication/270893248_SCENARIOS_FOR_WASTE-TO-ENERGY_USE-SWEDISH_PERSPECTIVE.
102. Chimenos JM, Fernandez AI, Nadal R, Espiell F (2000) Short-term natural weathering of MSWI bottom ash. Journal of Hazardous Materials 79: 287-299.
103. Bie R, Chen P, Song X, Ji X (2016) Characteristics of municipal solid waste incineration fly ash with cement solidification treatment. Journal of the Energy Institute 89: 704-712.
104. Verbinnen B, Billen P, Van Caneghem J, Vandecasteele C (2017) Recycling of MSWI Bottom Ash: A Review of Chemical Barriers, Engineering Applications and Treatment Technologies. Waste Biomass Valorization 8: 1453-1466.
105. (2015) Bottom ash fact sheet. CEWEP https://www.cewep.eu/wp-content/uploads/2017/09/FINAL-Bottom-Ash-factsheet.pdf.
106. R, De Brito J, Lynn C, Dhir RK (2017) Use of municipal solid waste incineration bottom ashes in alkali-activated materials, ceramics and granular applications: A review. Waste Management 68: 207-220.
107. Maria de Lurdes L (2019) Innovation in circular economy and new materials-FEUP. Science meeting 19.
108. Haiying Z, Youcai Z, Jingyu Q (2011) Utilization of municipal solid waste incineration (MSWI) fly ash in ceramic brick: Product characterization and environmental toxicity. Waste Management 31: 331-341.
109. Tang P, Chen W, Xuan D, Cheng H, Poon CS, et al. (2020) Immobilization of hazardous municipal solid waste incineration fly ash by novel alternative binders derived from cementitious waste. Journal of Hazardous Materials 393: 122386.
110. Biganzoli L, IIyas A, van Praagh M, Persson KM, Grosso M (2013) Aluminium recovery vs. hydrogen production as resource recovery options for fine MSWI bottom ash fraction. Waste Management 33: 1174-1181.
111. Mulder E (1996) Pre-Treatment of MSWI fly ash for useful application. Waste Management 16: 181-184.
112. Mao Y, Wu H, Jia M, Che X (2020) Pretreatment of municipal solid waste incineration fly ash and preparation of solid waste source sulphoaluminate cementitious material. Journal of Hazardous Materials 385: 121580.
113. Chimenos J, Fernandez LA, Cervantes A, Miralles L, Fernández M, et al. (2005) Optimizing the APC residue washing process to minimize the release of chloride and heavy metals. Waste Management 25: 686-693.
114. Quina MJ, Bordado J, Quinta-Ferreira RM (2014) Recycling of air pollution control residues from municipal solid waste incineration into lightweight aggregates. Waste Management, 34: 430-438.
115. Rémond S, Pimienta P, Bentz DP (2002) Effects of the incorporation of Municipal Solid Waste Incineration fly ash in cement pastes and mortars: I. Experimental study. Cement and Concrete Research 32: 303-311.
116. Shi HS, Kan LL (2009) Characteristics of municipal solid wastes incineration (MSWI) fly ash–cement matrices and effect of mineral admixtures on composite system. Construction and Building Materials 23: 2160-2166.
117. Joseph AM, Snellings R, Nielsen P, Matthys S, De Belie N (2020) Pre-treatment and utilisation of municipal solid waste incineration bottom ashes towards a circular economy. Construction and Building Materials 260: 120485.
118. Garcia-Lodeiro I, Carcelen-Taboada V, Fernández-Jiménez A, Palomo A (2016) Manufacture of hybrid cements with fly ash and bottom ash from a municipal solid waste incinerator, Construction and Building Materials 105: 218-226.
119. Juric B, Hanzic L, Ilic R, Samec N (2006) Utilization of municipal solid waste bottom ash and recycled aggregate in concrete. Waste Management 26: 1436-1442.
120. Zhang T, Zhao Z (2014) Optimal Use of MSWI Bottom Ash in Concrete. Int J Concr Struct Mater 8: 173-182.
121. Bertolini L, Carsana M, Cassago D, Curzio AQ, Collepardi M (2004) MSWI ashes as mineral additions in concrete. Cement and Concrete Research 34: 1899-1906.
122. Keppert M, Siddique JA, Pavlík Z, Cerny R (2015) Wet-Treated MSWI Fly ash used as supplementary cementitious material. Advances in Materials Science and Engineering 1-8.
123. Batista João Pedro Bittencourt (2018) Study of sugarcane leaf ash in alkaline-activated binders based on red ceramic waste. São Paulo: Paulista State University https://repositorio.unesp.br/handle/11449/157495.
124. Tonholo LFD, Azevedo AGS, Strecker K (2019) Corrosion study in geopolymers based on fly ash. IX Engineering Congress of the Federal University of São João del-Rei 2: 121444.
125. Davidovits J (2008) Geopolymer Chemistry and Applications. 5a edition. Saint-Quentin – France, Geopolymer Institute.
126. Guo S, Dai Q, Si R (2019) Effect of calcium and lithium on alkali-silica reaction kinetics and phase development, Cement and Concrete Research 115: 220-229.
127. Hon Loong L, Wendy PQ, Rex TL, Ern Huay, Abdul AMK, et. al. (2013) Green strategy for sustainable waste-to-energy supply chain. Energy 57: 4-16.
128. Ma C, Zhao B, Guo S, Long G, Xie Y (2019) Properties and characterization of green one-part geopolymer activated by composite activators. Journal of Cleaner Production 220: 188-199.
129. Mehrab N, Taghvaee VM (2022) Alkali-Activated Materials and Geopolymer: a Review of Common Precursors and Activators Addressing Circular Economy. Circular Economy and Sustainability.
130. Palomo A, Palacios M (2003) Alkali-activated cementitious materials: Alternative matrices for the immobilisation of hazardous wastes: Part II. Stabilisation of chromium and lead. Cement and Concrete Research 33: 289-295.
131. Yuan X, Chen W, Lu Z, Chen H (2014) Shrinkage compensation of alkali-activated slag concrete and microstructural analysis. Construction and Building Materials 66: 422-428.
132. Zhang P, Wang K, Li Q, Wang J, Ling Y (2020) Fabrication and engineering properties of concretes based on geopolymers/alkali-activated binders - A review. Journal of Cleaner Production 258: 120896.