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Management and valorisation of wastes through use in producing alkali-activated cement materials

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Abstract

There is a growing global interest in maximising the re-use and recycling of waste, to minimise the environmental impacts associated with waste treatment and disposal. Use of high-volume wastes in the production of blended or novel cements (including alkali-activated cements) is well known as a key pathway by which these wastes can be re-used. This paper presents a critical overview of the urban, agricultural, mining and industrial wastes that have been identified as potential precursors for the production of alkali-activated cement materials, or that can be effectively stabilised/solidified via alkali activation, to assure their safe disposal. The central aim of this review is to elucidate the potential advantages and pitfalls associated with the application of alkali-activation technology to a wide variety of wastes that have been claimed to be suitable for the production of construction materials. A brief overview of the generation and characteristics of each waste is reported, accompanied by identification of opportunities for the use of alkali-activation technology for their valorisation and/or management.

Keywords: Engineering; Immobilisation; Clean processes; Recycling; Waste treatment and waste minimisation

Contents

1. Introduction

Over the past decades, extensive discussions about climate change have taken place around the world, analysing its potential implications for the way in which our society works, especially for the vulnerable populations in less developed regions. Within this discussion, there is a growing consensus that climate change is not just an issue of energy efficiency or industrial carbon emissions, as our approach to demanding development and economic growth has proven to be highly unsustainable in an ecological sense.[1] Therefore, there is an urgent need to develop new and sustainable approaches to the manufacture and consumption of materials as a key component of the move to minimise waste generation. This also requires maximising the conversion of wastes into valuable resources. Figure 1 presents some concepts related to the (current and potential) implementation of closed-loop material flows in the construction industry, focusing specifically on urban and agricultural (rather than broader industrial) wastes, and the relationships between different industry sectors and waste generators of relevance in this context. Various wastes highlighted in Figure 1 (shaded in grey) are currently under-utilised or simply discarded, but offer potential for further valorisation through alkali-activation, and will form part of the focus of this review.

Across modern society, concrete is the second-most widely used material of any kind (after water),[2] as it is the pillar of the infrastructural development of our society and the basis of a large fraction of the global built environment. Modern concrete is mainly composed of hydrated Portland cement (which acts as the binding phase in more than 98% of all concrete produced worldwide) along with natural sand and rocks, and the engineering properties of the concrete as a whole are largely controlled by the chemistry and design parameters of the binder. However, Portland cement is not the only type of binder which can be used in concrete.[3] In the past decade, there has been rapid growth in international research efforts in the utilisation of wastes as alternative construction materials. One area of particularly rapid development has been the field of alkali-activated or "geopolymer" cements, where the reaction between an alkali source (referred to as the activator) and an aluminosilicate powder (referred to as the precursor) yields a hardened binder with performance (and often also appearance) similar to that of Portland cement,[4] but with a fraction of the CO_2 emissions.[5]

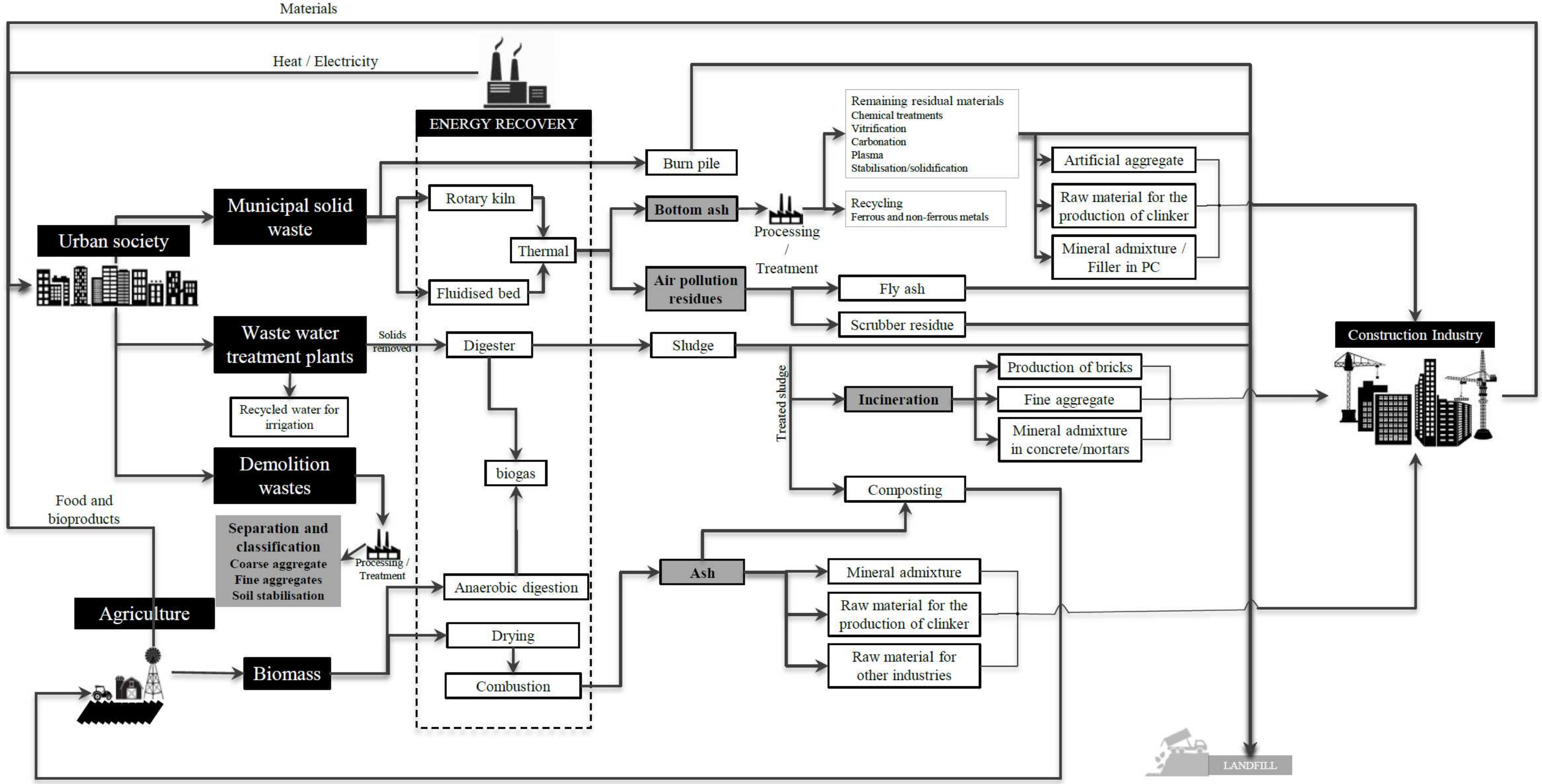

Figure 1. Schematic representation of some of the material flows related to recycling in the construction materials industry, focused on wastes generated directly by urban society and agriculture. Wastes identified in this review as having potential for use in alkali-activation are shaded in grey.

Precursors which are generally used in research and in the current (relatively early) stages of commercialisation of alkali-activated cements include industrial by-products such as fly ash from coal combustion, and slags from iron-making processes;[6] however, alkali activation can be applied to any material with a sufficiently high content of reactive Al_2O_3 and SiO_2 species. In recent years, there has been significant growth in the use of different urban, industrial and mining wastes as precursors for production of alkali-activated materials, as the high existing demand for blast furnace slag and fly ash in blends with Portland cement represents one of the main barriers to the further deployment of alkali-activated cements on a large industrial scale.[7] However, there does exist the need to increase the valorisation of some such wastes, especially for fly ash where the re-use rate can still be low: India, Middle East and Russia currently report fly ash utilisation rates of ~14%, ~11%, and ~19%, respectively.[8] There is also growing interest in the stabilisation/solidification of hazardous wastes via alkali-activation, to reduce the severe environmental impacts which can be associated with their chemistry and toxicity.[9,10]

In this paper, we present an overview of some of the wastes that have been used as precursors for the production of alkali-activated materials, the main material properties obtained when using those wastes in alkali-activation, and the associated development opportunities. Coal fly ashes and metallurgical slags will not be covered in detail, as their use in alkali-activation has been described in depth in recent reviews including.[4,11] High quality coal fly ash and ground granulated blast furnace slag are also in high demand for blending in Portland-based cements and concretes, which brings an associated cost, and thus many of the likely opportunities for growth in low-cost alkali-activated material production may be identified as being linked to precursors which are not currently used in standardised Portland cement blends.[12] The wastes to be discussed in detail here are outlined in Figure 2, which represents their approximate compositions on the CaO-SiO_2-Al_2O_3 ternary phase plane. Based on their chemical compositions, content of amorphous phases and degree of reactivity (which are all inter-related), the potential valorisation of these wastes through alkali activation can be addressed through two general alternative pathways:

1. Use the waste as main precursor for the production of an alkali-activated binder for sale as a product in its own right, or

2. The use of alkali activation technology to develop a new outlet for a particular

waste, including as an alternative source of SiO_2 in the alkali activator, as a secondary precursor or blending agent, or even as an aggregate.

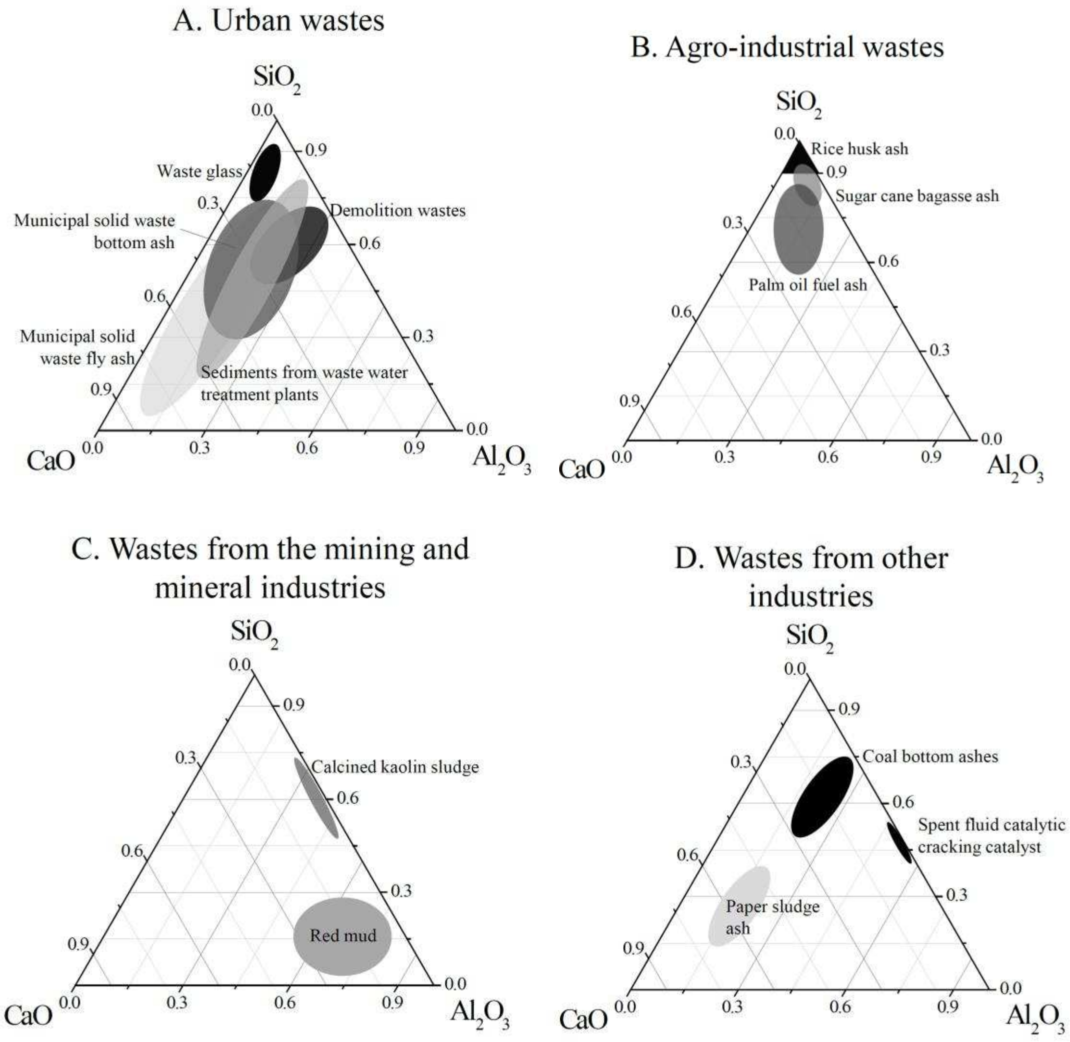

Figure 2. Approximate compositions of the wastes discussed in this review.

A key point that is generally neglected in academic studies is the volume of material available in any particular location for the production of cements or concretes. Cement and concrete are generally produced in very large quantities (up to hundreds of thousands of tonnes per annum) from a specific production site, and so any process for their production based on wastes needs to have a long-term secure supply of the waste of at least tens of thousands of tonnes per annum. This also needs to be secured on a time horizon of multiple decades, to enable recovery of the capital cost of construction of the production facility and an economically viable degree of profitability. Academic studies based on a single waste source rarely consider such aspects of scale-up when promoting the use of a particular waste as a precursor for alkali-activated cements, and so this paper will aim to provide some insight where possible, regarding these issues.

2. Urban wastes

2.1 Ashes from municipal solid waste incineration

The local and central authorities of urban and rural areas worldwide are currently under pressure to find responsible ways to manage and dispose of the municipal solid waste (MSW) that is produced every day. China alone generates over a quarter of total global MSW (~250 Mt/y), with a reported annual growth rate of 8 to 10%,[13] as a consequence of its growing urbanisation and consumer-focused society. Landfill is the main strategy for MSW management in China, and only ~15% of municipal wastes are incinerated.[14] In the U.S., the MSW that is recyclable is less than ~35% of total MSW arisings,[15] and the non-recyclable wastes are landfilled, as this is an easy and currently inexpensive method for disposal.

Landfilling of MSW has severe environmental impacts including odour emissions, groundwater pollution from landfill leachate, and soil contamination. Therefore, the controlled incineration of municipal solid wastes (MSW) has become a more widespread way used to manage this kind of wastes. By direct incineration of MSW, it is possible to reduce the volume of waste by converting it into an ash (achieving up to 80-90% volume reduction depending on the nature of the waste), and decrease the amount of waste that needs to be landfilled,[16] with the added value that the energy recovered from the heat that is released during the incineration of plastics, paper, other organic matter, and ferrous and non-ferrous metals can have significant financial value.

The main disadvantages associated with MSW incineration are the high levels of emissions of greenhouse and other problematic gases, and the large amounts of ashes which can be generated.[17] These ashes can be categorised essentially into two groups: bottom ash (BA-MSW), which is the material that remains in the furnace after combustion, and the air pollution control residues that are removed from the flue gas.[18] The BA-MSW represents ~80% of the total residues generated during incineration [19,20]. Scrubber residues are retained by sorbents (such as lime or sodium hydroxide), and the fly ash (FA-MSW) is separated by filters or electrostatic precipitators [18], as shown in

Figure 3. Figure 4 shows a scanning electron microscope (SEM) micrograph of a particle of FA-MSW, which depicts its heterogeneous, highly porous structure and a particle size of around 50 μm.

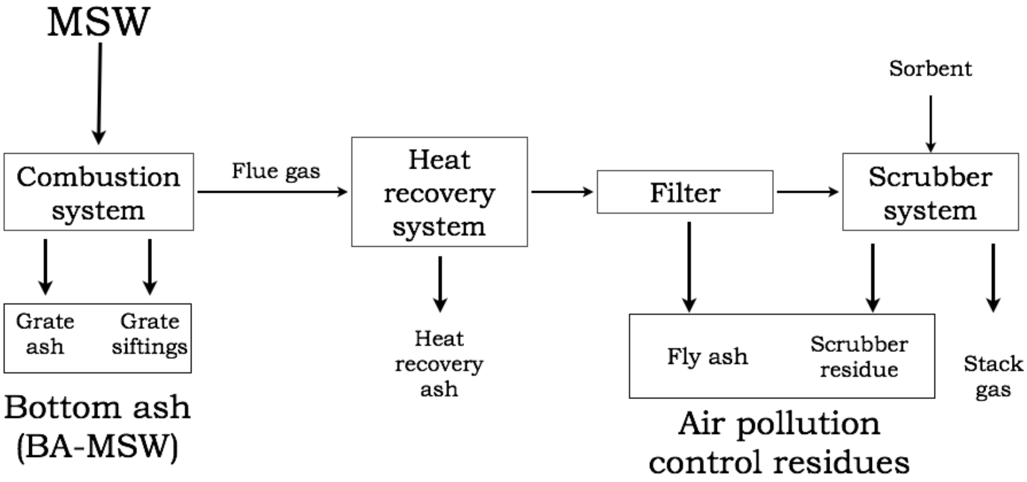

Figure 3. Basic unit operations and mass flows of an MSW incineration plant.[18]

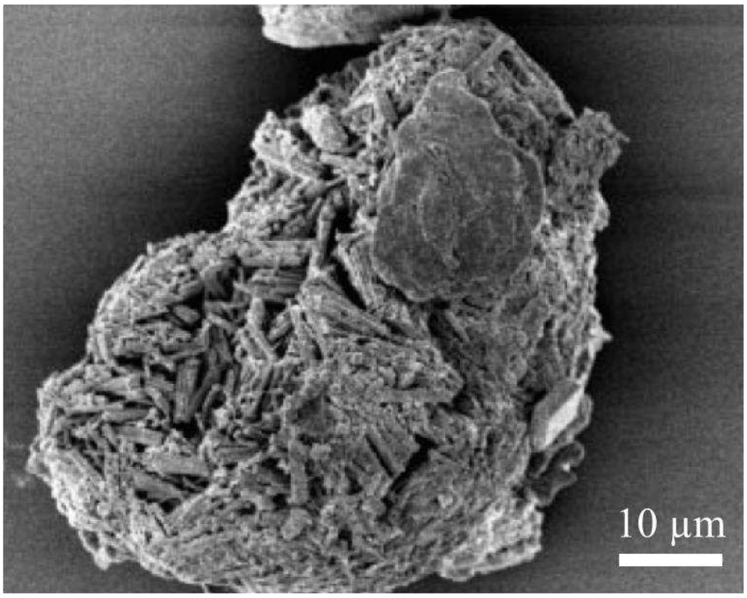

Figure 4. SEM image of a particle of FA-MSW showing the heterogeneous nature of this waste even within a single particle, and the intraparticle porosity. From Kersch et al.[21], copyright John Wiley & Sons.

MSW ashes are often classified as hazardous due to the presence of toxic elements and organic compounds, and consequently these ashes must be treated and disposed with care, considering regulatory aspects and specifications such as the European Waste Catalogue List (19 01).[22] The major elements present in MSW ashes are mainly O, Si, Ca, Al, Fe, Na, and K. BA-MSW also has carbon due to unburned material. Although most of the metals are present as oxides, there are also considerable quantities of metal chlorides, metal sulfates and metal carbonates, and some non-oxidised metallic components. Some ashes may also contain significant amounts of polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), chlorobenzenes, chlorophenols, chlorinated compounds, benzofurans or mutagenic organic chemicals.[23] When the MSW ashes are used by the construction industry or as geotechnical materials, the leachability of these organics, as well as alkalis and heavy metals, is a major concern, as these can affect the properties of the concretes and the soils. Ashes with high chloride content are also severely restricted from usage in reinforced concretes due to the risk of corrosion of the embedded steel reinforcement.

Currently, the utilisation of ashes from MSW combustion is very limited, especially if the ash has not been pre-treated, and also due to the intrinsically high variability of this type of ash. Some ashes are decontaminated by different processes, including wet chemical treatment,[24] thermal or plasma vitrification,[25,26] carbonation,[27] or disposed via stabilisation/solidification (S/S) in a cementitious matrix.[18] Life cycle analysis has enabled quantification of the environmental benefits associated with the re-use, particularly metal recovery, of the MSW ashes; a significant reduction is observed related to the global warming impacts.[28]

The recycling of MSW ashes by the construction industry has increased worldwide over the past years, including the assessment and use of FA-MSW and BA-MSW as aggregates,[29–32] as raw materials for Portland clinker production, [33,34] and as mineral admixtures for the production of concretes.[35] Some studies have identified that the presence of slowly-reacting siliceous glass or metallic aluminium particles in the ashes derived from MSW might negatively affect the durability properties of cements and concretes, as these components can increase the susceptibility to degradation, via the alkali-silica reaction or the release of hydrogen gas, respectively.[29,36]

The stabilization/solidification (S/S) of MSW ashes via alkali-activation has also been assessed. The mechanisms of heavy metal immobilisation in an alkali-activated binder can be physical and/or chemical, where the hazardous elements are either fixed in the gel network, linked into the structure in change balancing roles, or physically trapped in a dense and low-permeability matrix.[37] Luna-Galeano et al.[38] studied FA-MSW incorporation into alkali-activated systems based on a variety of precursors (including metakaolin, blast furnace slag and coal combustion fly ash) and alkali activators (sodium and potassium hydroxide and silicate). Although the mechanical performance of the wasteforms produced was relatively low (< 10 MPa after 28 days), the leachability of Zn, Co, Ni and Sn was greatly reduced compared to the raw MSW ash. Lancelloti et al.[39] showed that metakaolin-based systems can stabilise larger amounts of MSW ashes when compared with conventional cementitious S/S.

The use of untreated MSW ash as a precursor in the production of alkali-activated binders is limited due to its toxicity and the low contents of amorphous, reactive SiO_2 and Al_2O_3-containing phases. However, some MSW residues have been shown to be suitable to be used in this way[40,41]; Zheng et al.[41] achieved compressive strengths of up to 20 MPa after 7 days of curing for such materials. The use of CaO for flue gas treatment in MSW incineration facilities generates fly ashes rich in Ca-compounds ($Ca(OH)_2$, $CaCO_3$, or $CaSO_4$)[42], and these can be beneficial for strength development and permeability reduction in alkali-activated binders. Some FA-MSW materials can be treated by washing to reduce the content of undesirable elements such as Cl, Zn, Cu, Cr, Pb, Cd and Ni. Zheng et al.[40] also reported that after a washing treatment, an FA-MSW exhibited higher reactivity in alkali-activation, yielding a binder with improved mechanical performance due to the removal of the chloride which was affecting setting and mechanical performance.[43,44] This was consistent with the results of Ferone et al.[45], who evaluated the effect of blending fly ash with FA-MSW which had been pre-washed to remove both chloride and sulfate, and found an improvement in terms of leaching performance. However, the washing process does itself generate a secondary liquid waste stream which requires further treatment, and this added cost must be considered when assessing the desirability of the washing step in waste treatment.

Diaz-Loya et al.[46] assessed alkali-activated systems based on blends of coal FA and FA-MSW. Their materials based solely on FA-MSW showed leachability of heavy metals (with the exception of Se) which was within the allowable limits according to the US Environment Protection Agency. The alkali-activated binders containing 60% FA-MSW exhibited mechanical performance which was suitable for the production of non-structural precast products: a compressive strength of 18 MPa and flexural strength of 2.8 MPa after curing at 100 ºC for 7.

In general, unless a decontamination treatment is applied, the use of MSW ashes as a raw material for alkali-activated cements in civil construction applications seems limited, as the products may not comply with the toxicity regulations to be used as a building material, and will tend to be variable in quality and performance. In this sense, MSW ashes present challenges related to valorisation as a construction material via alkali-activation, and future work in this area is likely to be driven predominantly by environmental arguments and the need to avoid landfilling of the waste ash, rather than any particularly desirable or unique technical properties of the materials produced. However, it does seem that solidification/stabilisation using alkali-activated matrices may be a viable route for the management of this waste via incorporation into a solid binder rather than simply landfilling it, as such a process can contribute significantly to reducing the leachability of toxic elements to the environment.

2.2 Demolition and ceramic-type wastes:

Roughly 45% of the total wastes arising from construction processes are ceramic-type wastes[47], which are produced from two main sources:

- **Wastes generated by demolition and construction activities:** including construction and demolition wastes: concrete, bricks, roof tiles and ceramic materials.
- **Wastes generated by the ceramic industry**: including waste from thermal processes or from the manufacture of bricks, roof tiles and construction materials.

These wastes are generally classified as non-hazardous,[22] as long as no asbestos is present. According to Dahlbo et al.,[48] the current construction and demolition waste management system of the European Union needs to be significantly updated and modified in order to achieve the target of recycling a minimum of 70% in 2020 as suggested by the EU Waste Framework Directive (2008/98/EC). However, the main problems in the utilisation of wastes generated by demolition and construction materials are related to the lack of control of composition (which is very heterogeneous) and the difficulty in extracting certain contaminants, e.g. wood, paper, gypsum, glass, rubber, among others.[49] Europe and the U.S. have made significant advances over the past decades in the correct classification and subsequent reuse of construction wastes. New techniques to ensure effective separation, instead of selective demolition and manual sorting, are now utilised, such as wet jigging,[50] air jigging,[49] heavy liquid separation,[51] optical sorting and near-infrared sorting technology[52].

The main consumer of these wastes is the same construction industry which generates them, and common applications include soil stabilisation, use as a fill material for landscaping, as an artificial aggregate in the production of concrete, and/or use as a raw material for the production of Portland cement.[53–56] However, in growing economies where high volumes of ceramic and demolition wastes are generated, the potential for recycling and re-use of these wastes is often not reached as a consequence of the low cost and high volume availability of virgin raw materials, as well as the limited expertise available for treating wastes and the limited allocation of resources for waste management. Recently, life cycle analysis modelling has demonstrated that the re-use and valorisation of construction and demolition wastes can reduce the footprint of the industry across most environmental impact categories.[57,58] However, transportation is the most important impact to be considered; its contribution to the global warming impacts can be high, and may in fact dominate other benefits if local valorisation is not possible.[58]

The use of demolition wastes for the production or development of alkali-activated cements is challenging, considering the varying nature of these wastes and the consequent lack of consistency in chemical and physical properties across wastes from different sources. There is also a high energy and financial cost associated with the reduction of wastes to a sufficiently fine particle size for use as a precursor in alkali-activation, as crushing to a particle size in the range of tens of microns is very much more expensive than when targeting a normal aggregate particle size (a few millimetres to a few centimetres), and problematic dust emissions may also be associated with this process.

However, there do exist reports related to the use of demolition wastes as a precursor for production of alkali-activated cements. For example, Payá et al.[59] assessed hydrated Portland cement which had previously been carbonated in an attempt to replicate end-of-life conditions for cement in regular concretes, by alkali-activation with NaOH and waterglass. Their mortar specimens cured at 65 ºC after 3 days exhibited a compressive strength on the order of 10 MPa, demonstrating potential use of cement-rich fraction of the demolition wastes, which is not strongly desirable as an aggregate due to its high water demand in concrete mixtures. The applicability of cement recovered from demolition wastes as a precursor for alkali-activated materials is likely to be limited by competition from the re-use of this material in Portland cement clinker manufacture, and so further assessment will be required to elucidate the true feasibility of this option from financial, technical and environmental points of view. Recently, Komnitsas et al.[60] demonstrated the potential use of construction and demolition wastes (including recycled concrete, bricks and tiles) as raw materials for the synthesis of geopolymers: high mechanical strength (> 40 MPa after 7 days of curing) was achieved under specific synthesis conditions using wastes derived from tiles and bricks. However, the demolition wastes based on recycled concrete (regardless of the particle size distribution) showed a lower degree of reactivity and lower mechanical performance. These results elucidate the importance of developing an effective selection and screening process for the demolition wastes prior to use as a precursor in alkali-activation, taking into account their heterogeneity.

Therefore, the wastes generated by the ceramic industry can probably be reused more easily than general demolition wastes due to the greater control of composition, and thus reduced variability. The largest producers of clay-based ceramic tiles are China, Brazil, India, Italy, Iran and Spain, which together represent ~70% of global production,[61] and in these countries, the residues generated during the production of ceramic products are mainly disposed in landfill. These ceramic wastes consist mainly of silicate and aluminosilicate minerals obtained through the calcination of clays, such as quartz (SiO_2), feldspars ($MAlSi_3O_8$ where M is an alkali metal) and vitreous phases. Several studies have described[62,63] the use of these ceramic wastes as a coarse or fine aggregate for concrete or mortar production, or as a raw material for the production of Portland clinker.[64,65]

Some ceramic wastes do show pozzolanic reactivity, as they contain amorphous aluminosilicate phases which react with the portlandite formed during the hydration of Portland cement.[66–69] Although the pozzolanicity of these wastes is significantly lower than that of other calcined clays (such as metakaolin), their value as precursors in alkali-activated cement production can be optimised through control of the formulations and the activation conditions. Reig et al.[47,70] evaluated the alkali-activation of an aluminosilicate waste obtained from red clay bricks and porcelain stoneware; mortars cured at 65 ºC for 7 days developed compressive strengths exceeding 20 MPa, demonstrating that it might be feasible to reutilise these wastes for the production of alkali-activated cements. Allahverdi and Najafi Kani [71] produced alkali-activated pastes based on blends of waste bricks and 8-month old crushed concrete, which achieved compressive strengths of up to 40 MPa after 28 days of curing.

The use of recycled crushed material obtained from bricks and other clay products as raw materials for the development of alkali-activated cements is currently quite limited, although studies including those described above suggest that it may be technically achievable. One of the main limitations in a practical sense is the low volume of production of clay-based demolition waste in any particular location, compared with what might be commercially required for production of alkali-activated cements at an industrial scale, as most activities which generate such wastes are small in scale. Likewise, the growing demand for low-cost housing in many areas around the world has led to the development of improvised brick factories, whose product control is minimal, which can consequently affect the potential reactive quality of the powdered brick after recycling.

Conversely, ceramic wastes such as broken or off-specification porcelain stoneware, tiles, tableware and others, that can be sourced directly from the factories manufacturing these products rather than from the demolition process, could have higher potential as precursors for alkali-activated cements, as the raw materials and process of manufacture are well known, and there will be greater consistency in the properties of the wastes to enable optimisation of alkali-activated cement formulations. This is an interesting area of research that needs to be further explored, although the volumes of these wastes available from each single source tend to be rather small compared to the scale of cement production facility throughput values, and so such products may be best utilised in niche products such as refractories,[72] which can make use of their intrinsically high thermal resistance, rather than in production of bulk construction materials.

2.3 Wastes or sediments from water treatment plants

Sewage sludge is a residue generated by the wastewater treatment process, where the liquid and solids fractions are separated. Residues are collected during the primary (physical and/or chemical), secondary (biological) and tertiary (nutrient removal) treatment. The solids collected can be subjected to further treatments (including biological, thermal, long-term storage, among others) and are finally disposed. The quality of the sludge produced is affected by the degree of pollution of the effluent treated and the technical features of the water treatment plant. The physical and chemical processes involved in sewage sludge treatment tend to increase the concentrations of heavy metals, such as Zn, Cu, Ni, Cd, Pb, Hg and Cr,[73] as water is progressively removed from the sludge. In Europe, 35-45% of the sewage sludge generated is still landfilled, 37% is used in agriculture, 11% incinerated and the remainder is used in other areas such as forestry and land reclamation.[74] The presence of hazardous compounds restricts the use of sewage sludge in agriculture due to its potential ecotoxicity, and therefore it has to be assessed carefully before utilisation, to reduce any harmful effects.[75]

There exist some reports related to the co-combustion of sewage sludge in cement manufacturing, where the calorific power of the organic fraction of the sludge is used as a source of energy. The main restriction in blending the sludge with coal for combustion within the kiln is the emission of harmful elements, including heavy metals which can accumulate in the cement kiln dust. On other hand, the ashes generated during the incineration of sludge wastes have been used in the construction industry as a fine aggregate, as a mineral admixture in concrete/mortars mixes,[76] or as a raw material for the production of bricks.[77,78] There do not exist reports related to the assessment of sewage sludge ashes as the sole raw material in the production of alkali-activated cements, as these ashes tend not to contain high contents of reactive aluminosilicates; instead, alkali-activated cements have been examined as potential solidification/stabilisation matrices for these ashes, to reduce the leachability of heavy metals.

Yamaguchi and Ikeda[79] evaluated the solidification of sewage sludge slag, which is produced via the melting of the sludge at high temperature, in a fly ash based geopolymer matrix. It was identified that the sewage sludge slag was an ‘active filler’ and the best mechanical strength was obtained at a 25 wt.% sludge slag loading, although high temperature curing (80 °C) was required to produce monoliths. Such slags could potentially be utilised in the production of alkali-activated matrices, but further research in this area would certainly be required, especially regarding immobilisation of heavy metals.

Reservoir sludge is a by-product resulting from the storage and treatment of potable water, mainly consisting of deposited clays and silt, and thus contains much lower levels of toxic substances than sewage sludge. It can therefore be categorised in most cases as a non-hazardous waste and may be reused in different engineering applications. Taking into account its relatively high content of clay minerals, reservoir sludge can be thermally treated to produce bricks or lightweight aggregates,[80] or blended with other precursor materials as a reactive component of an alkali-activated binder system. It has been demonstrated[81] that the compressive strength of ternary alkali-activated binders with 30 wt.% blast furnace slag, 20 wt.% metakaolin and 50 wt.% calcined reservoir sludge increases significantly when the sludge is thermally treated at 800-850 ºC, consistent with the thermal activation of the clay minerals present. The maximum compressive strength reported was 56 MPa after 28 days of curing, and the mechanical performance was reduced slightly when the content of the calcined reservoir sludge was increased. Foamed alkali-activated panels based on calcined reservoir sludge with 30% blast furnace slag have also been shown to generate valuable sound-insulation properties, as expected for a low-density material based on calcined clays, offering an alternative to the use of more expensive commercial metakaolin sources in such applications.[82]

The use of calcined reservoir sludge as the sole aluminosilicate component of an alkali-activated binder was evaluated by Ferone et al.,[83,84] using NaOH and waterglass solutions as alkali activators. The sediments were based on quartz, feldspar, kaolinite, illite and smectite, and after being thermally treated at up to 750 ºC and combined with the alkali activator, the materials developed compressive strengths lower than 12 MPa after 3 days at 60 ºC. Strength development was improved greatly (38 MPa under the same conditions) when some blast furnace slag was added as a more reactive secondary constituent of the binders.

Alkali-activation seems to be a suitable technology for exploiting reservoir clay sediments, which do not currently have commercial value. It is important to note that the variation in clay content and nature means that mix design optimisation (including blending with other aluminosilicate materials) will be needed in each location rather than using a single universal ‘ideal’ formulation. However, alkali-activation technology seems to be a suitable alternative for the manufacture of valuable products from these wastes.

2.4 Waste glass

The rates of production and consumption of glass for packing differ widely between countries, and so in some countries a very high degree of reuse or recycling of waste glass is achieved, while in others (particularly countries which are high-volume importers of wine), there are a lot of waste glass bottles generated which are not suitable for domestic re-use. In EU, the glass packing waste generated was 32 kg per capita in 2011. Although the 2008 target of 55% waste glass (WG) recycling has been achieved by most EU Member States, there still exists scope to increase the recycling and recovery rate.[85] The non-recyclable mixed-colour broken glass from used bottles, along with the glass from fluorescent lamps, can represent an environmental problem for municipal waste treatment plants as the glass is not biodegradable, and landfilling is not making effective environmental or economic use of the value and energy embodied in these residues. According to Vossberg et al.X, glass recycling shows significant energy savings (>25%) and greenhouse gas emissions reduction (~35%) when compared to landfilling.[57]

The efficiency of the glass recycling process is strongly affected by the collection method and the ability to sort the glass by colour. If glasses of different colours are correctly separated, they can be used many times without significant changes in chemical or optical properties. However, when coloured glasses are mixed, they are not suitable for reuse and then are disposed mainly in landfills. Additionally, although used fluorescent lamps are typically processed to remove the mercury and reduce its concentration to the levels recommended by the Waste Acceptance Criteria (<0.2 mg/kg),[86] the growing adoption of fluorescent lighting systems is making difficult the safe disposal and recycling of the full range of lamps available on the worldwide market.

The use of waste glass in Portland cement production has generally been avoided, as it increases the alkali content in the clinker, which can generate alkali-aggregate reactions as well as the potential for flash setting due to the formation of highly soluble sulfate salts.[87] The use of waste glass as a partial replacement of coarse or fine aggregate in the production of concrete is also limited, again due to the reaction induced between the reactive silica present in the glass and the alkalis of the Portland cement (and the glass itself). However, when the waste glass is crushed and pulverized to smaller than 300 µm, and aluminous supplementary cementitious materials such as coal fly ash are used, the deleterious effect attributed to the alkali-silica reaction decreases.[88,89] Some very finely ground waste glasses show pozzolanic activity, and they can be used for the partial replacement of Portland cement for concrete production, as they may enhance mechanical performance.[90]

In the context of alkali-activation of waste glasses, two main approaches have been investigated: use of the waste glass as a solid precursor for the alkali-activated cement, or as a raw material for the production of low cost sodium silicate solutions. In utilising waste glass as a precursor for alkali-activated cement production, Cyr et al.[91] assessed the use of a green soda-lime-silica waste glass activated by alkali hydroxide solutions, and obtained mortars with a compressive strength of up to ~60 MPa after 56 days of curing. As the content of SiO_2 in the waste glass was quite high (~72%), the use of a silicate activator was not necessary to achieve high compressive strengths. The absence of a sodium silicate-based activator significantly reduces the cost of production of these materials.

Redden et al.[92] carried out a comparative study activating glass powder, fly ash, and blends of these materials, and identified that the glass powder-based activated cements developed higher strengths than activated fly ash cements when cured at room temperature. However, the main reaction product of glass activation was a sodium silicate gel, which was highly soluble in water and alkaline media, calling into question the stability of these cements in a real service environment in the absence of an added aluminium or calcium source that could generate an insoluble gel. Avila-López et al.[93] utilised urban waste glass, blended with limestone as a low-cost source of calcium, to produce alkali-activated cements. Higher reactivity of the waste glass was identified when using NaOH as an activator, which promoted the formation of a C-S-H type gel along with the hydrous Ca-Na carbonate salt pirssonite as main reaction products. Compressive strengths of up to 38 MPa were obtained in optimised mixes.

Badanoiu et al.[94] synthesised foamed alkali-activated cements using waste glass cullet, red mud, and blends of these materials, activated by solutions of NaOH and liquor derived from the filtration of red mud slurry, with the aim of using waste-derived materials as both precursors and activators. These foamed cements developed a compressive strength of 25 MPa after curing at 60 °C for 24 h then at 20 °C and 85% relative humidity (RH) for 7 days.

These studies demonstrate that waste glasses can certainly be used as precursors for producing hardened alkali-activated cementitious materials. However, the mix designs need to be adjusted and optimised in order to produce stable reaction products, so that these cements can withstand service conditions, and therefore develop desirable durability.

Puertas and Torres-Carrasco have also demonstrated the production of sodium silicate solutions via chemical digestion in NaOH/Na_2CO_3 solutions of urban waste glasses,[95] and have used these solutions as alkali activator for producing cements based on alkali-activated slag,[96] and alkali-activated fly ash.[97] These studies have elucidated that waste glass can be recycled for production of sodium silicate solutions, and that these solutions can act as effective activators for producing alkali-activated cements, as similar compressive strengths and phase assemblages were identified when using these alternative activators compared with those obtained when using commercial sodium silicates. This seems to be a very viable alternative for the recycling of waste glass to produce a valuable product.

Other types of waste glass, such as solar panel residue glass,[98] have also been utilised in laboratory studies as a partial replacement material in metakaolin-based activated cements. Although material performance seemed acceptable on a lab scale, the applicability of such processes (or those including post-consumer glasses from electronic items such as display screen equipment) at an industrial scale is likely to be infeasible, considering the low volume availability of such residues worldwide or in any particular location; a very large (and expensive) number of broken panels or screens would be required to produce a useful quantity of concrete. However, as hazardous elements might be present in the waste glass, alkali-activation technology could be a suitable alternative for its safe disposal if the production of a monolithic wasteform is desired.

3. Agro-industrial wastes

3.1 Rice husk ash

Rice is a cereal grain, and is the most widely consumed staple food for a large part of the world. It is the third-highest produced crop worldwide (744 million tonnes in 2014[99]), after sugarcane and maize.[100] Every five tons of rice from paddy cultivation produce one ton of rice husk waste, and in 2014 alone more than 148 million tonnes of rice husk were produced worldwide. Currently, some rice husks are utilised as fuel, and the resulting ashes, Figure 5, are a low cost source of amorphous silica that has been extensively used by the construction industry as a supplementary cementitious material for concrete production.[101,102] The pozzolanic activity of a rice husk ash depends on its content of amorphous silica and unburnt carbon, the particle size distribution and specific surface area, all of which are strongly affected by the combustion temperature and duration.[101,103]

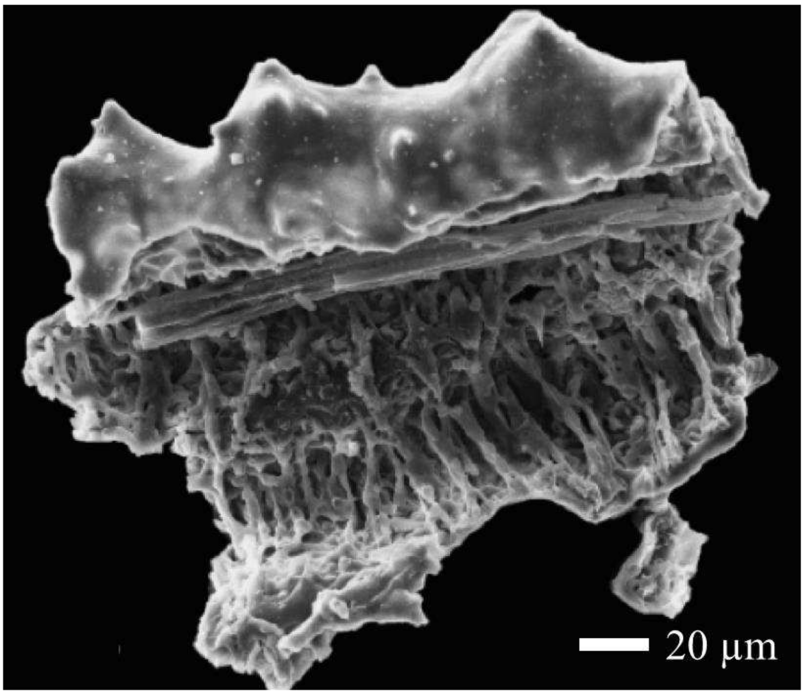

Figure 5. SEM micrograph of a rice husk ash particle, showing its porous structure which yields a high specific surface area and thus rapid reaction. From Abreu et al.,[104] copyright John Wiley & Sons.

In the context of alkali-activated cements, similar to the situation discussed in the preceding section for waste glasses, rice husk ash has been used both as a secondary precursor and as a silicate source for production of sodium silicate activating solutions.

Detphan et al.[105] used rice husk ash, produced at different combustion temperatures, as partial replacement material in alkali-activated coal fly ash cements. The rice husk ash fineness and the degree of fly ash replacement strongly influenced the compressive strength; mechanical strengths of up to 56 MPa were achieved when the rice husk ash was sintered at 690 °C and the amount of small particles increased. Rattanasak et al.[106] blended rice husk ash with $Al(OH)_3$ to produce alkali-activated cements, adding sodium hydroxide and sodium silicate as alkali activators. Boric acid was also added to these binders to reduce their solubility in water. The formation of an aluminosilicate type gel as the main reaction product in these binders was observed, with compressive strengths between 14 and 20 MPa after 90 days of curing, depending on the $Al(OH)_3$ content. This study elucidated that hardened solids containing more than 70 wt.% rice husk ash can be produced, and that these materials can achieve moderate but useful compressive strengths.

He et al.[107] assessed the compressive strength and microstructural features of red mud/rice husk ash blended alkali-activated cements, and identified that an increased content of red mud promoted the development of higher compressive strengths, depending on the formulation of the binders. As observed by Rattanasak et al.[106], an aluminosilicate type gel is forming in these cements, which is responsible for mechanical strength development over the time of curing.

Gastaldini et al.[108] produced blended concretes containing 80 wt.% Portland cement, 20 wt.% rice husk ash, and 1 wt.% of either Na_2SO_4, K_2SO_4 or Na_2SiO_3. An increase in the compressive strength development at early time of curing (7 days) was identified when alkali activators were included, along with a significant reduction in chloride permeability of the concretes.

The dissolution of rice husk ash into concentrated NaOH to produce sodium silicate solution as an alkali-activator is an attractive application of this waste in the field of alkali-activation technology. Bernal et al.[109] evaluated the effectiveness of this alternative activator in producing cements based on slag, metakaolin and their blends. This study elucidated that the mechanical performance and structural development of the alkali-activated cements produced with the waste-derived activator was comparable with the results obtained when using a commercial sodium silicate solution of corresponding chemical composition. Similar observations have been identified when using these alternative activators in producing alkali-activated cements based on coal fly ash/slag blends[110] or spent fluid catalytic cracking catalysts.[111]

The thermal resistance of alkali-activated slag cements produced with a rice-husk ash based activator has also been assessed,[112] with higher retention of compressive strength after treatment at up to 1000 °C than in comparable cements produced with a commercial silicate solution. Villaquirán-Caicedo et al.[113] observed the formation of different crystallisation products upon high temperature exposure of alkali-activated metakaolin binders based on waste-derived or commercial sodium silicate activators, which could influence the performance of these binders under fire conditions. This was associated with the differences in the speciation of the soluble silicates available during the activation reaction when using rice husk ash based or commercial sodium silicate solutions.

3.2 Palm oil fuel ash

Palm oil is now a significant bio-based energy source in many parts of the world, particularly in Southeast Asia, Africa and South America. The main wastes derived from the palm oil production process are shells, palm kernel cake and fibres, among others, which are often utilised as fuel for steam production in palm oil mills. During this combustion process, a large quantity of siliceous ash is produced, and over the past decades this has begun to be utilised as a partial pozzolanic replacement for Portland cement in producing concrete.[114–116] As in the case of other biomass ashes, the palm oil fuel ash particles exhibit heterogeneous shape, a cellular structure and high specific surface are (Figure 6), which increase water demand when used as a mineral admixture in cements and concretes.[116] Recent efforts have also focused on maximising the recycling of palm oil fuel ashes via alkali-activation, as there is a rapid growth in palm oil production, and interest in biomass combustion to produce electricity as a means of reducing the cost of disposal of these wastes.

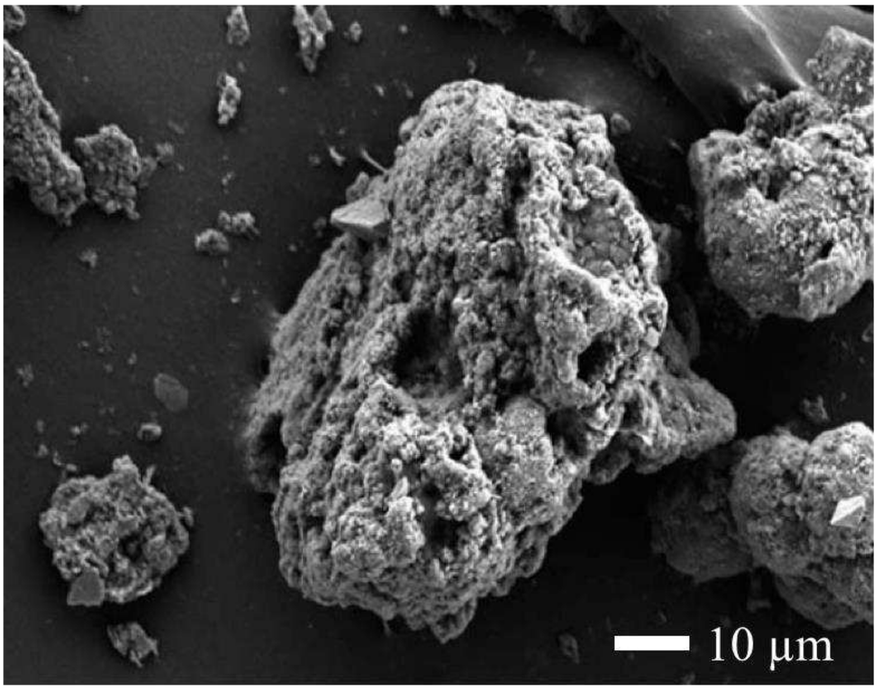

Figure 6. SEM image of a particle of palm oil fuel ash, showing the porous structure of the larger particles present. From Ooi et al.,[117] copyright John Wiley & Sons.

Most of these studies have been based on a single source of palm oil by-product ash, and have focused on the assessment of the effects of different mix design parameters on the strength development and basic microstructural features of alkali-activated cements based on palm oil fuel ash. However, this approach has meant that there is little broader generic information available regarding this class of ashes as a whole, as each study considers only the characteristics of a single material. There is a high degree of variability between palm oil fuel ashes in terms of composition and mineralogy, although most tend to be relatively low in reactive alumina content and thus challenging to use as a sole precursor for alkali-activated cements. Salih et al.[118] assessed the effect of the curing temperature and duration on the compressive strength development of these cements, identifying that comparable compressive strengths (21 - 24 MPa after 7 days) were obtained in samples cured at room temperature compared with specimens cured at between 60 °C and 80 °C. This elucidated that high temperature curing is not required for these cements, if the mixes are appropriately designed.

The utilisation of palm oil fuel ash as a secondary precursor for production of blended alkali-activated cements has also been widely studied, and the fineness of these ashes has a strong influence on reactivity and consequently strength development. Yusuf et al. produced alkali-activated cements[119] and concretes[120] based on blends of ultrafine palm oil ash and blast furnace slag. The addition of up to 20 wt.% ultrafine palm oil fuel ash to the slag-based mixes increased the compressive strength after 28 days of thermal curing, but higher volumes of ash slightly reduced mechanical performance. Conversely, Islam et al.[121] identified that the optimal level of blast furnace slag substitution by a coarser palm oil ash was 30 wt.%. Blended palm oil ash-slag alkali-activated cements exhibited good chemical resistance when exposed to sulfuric acid, when the content of slag was lower than 40 wt.% of the total binder (to minimise the degree of damage which could happen via decalcification and gypsum formation) and when the water content of the cement was held low.[122]

Ranjbar et al.[123,124] partially replaced coal fly ash by palm oil fuel ash in alkali-activated cements, where a delay in compressive strength development was observed as the fraction of palm oil fuel ash increased, in contrast to the trend identified in activated slag/palm oil fuel ash cements as noted above. These alkali-activated palm oil fuel ash/fly ash blended cements gained strength when exposed to temperatures of up to 500 °C and then cooled to room temperature for testing; however, larger fractions of palm ash reduced the strength retention upon heating of these materials. High resistance to sulfuric acid exposure was also found in concretes based on these binders by Ariffin et al.,[125] compared with Portland cement based concretes. This was again associated with the absence of Ca-rich reaction products, which are more prone to react with the sulfuric acid to form gypsum.

Kupaei et al.[126] identified an increase in the compressive strength of foamed cements as coal fly ash was partially replaced by palm oil fuel ash, which was attributed to the higher water demand of the coal ash and thus the need to add more water to achieve satisfactory workability, and Liu et al.[127] also developed low-density structural insulating materials from this combination of precursors. Hawa et al.[128] added palm oil fuel ash to alkali-activated metakaolin, which was able to decrease the tendency towards drying shrinkage of these alkali-activated cements.

The growing number of studies utilising this waste, and the positive results obtained in terms of mechanical performance and durability, elucidate that alkali-activation technology is a feasible pathway for its exploitation and the production of construction materials in palm oil producing areas, some of which are underdeveloped and in need of low-cost housing. The production volumes of palm oil fuel ash from major electricity generating facilities are also sufficient to make the production of alkali-activated concretes from the ash potentially economically viable, and the timescale on which these ashes are expected to be produced is also sufficiently long to make construction of dedicated facilities for their utilisation in construction materials appear worthwhile.

3.3 Sugar cane bagasse ashes

Sugar cane is the single most produced crop in the world,[100] with an estimated production of more than 2165 million tonnes in 2013,[129] around 30% of which is produced in Brazil, with very large volumes also generated in other warm-climate regions of the Americas and Asia. These regions in general correspond to areas of high demand for construction materials, and so any by-products generated by the sugar industry would appear to be geographically well located for use in concrete production. This is highlighted in Figure 7, which compares the per-capita cement and sugar cane production for the world's top 10 sugar cane producing countries. All of these nations have relatively high per-capita cement production, correlating well with sugar cane production (circled region) except in the cases of Brazil (high sugar cane, moderate cement) and China (high cement, moderate sugar cane) as marked in Figure 7. This indicates that there is generally likely to be good availability of sugar cane bagasse ash in areas of high demand for construction materials, which shows a strong potential for the valorisation of this waste material in construction applications.

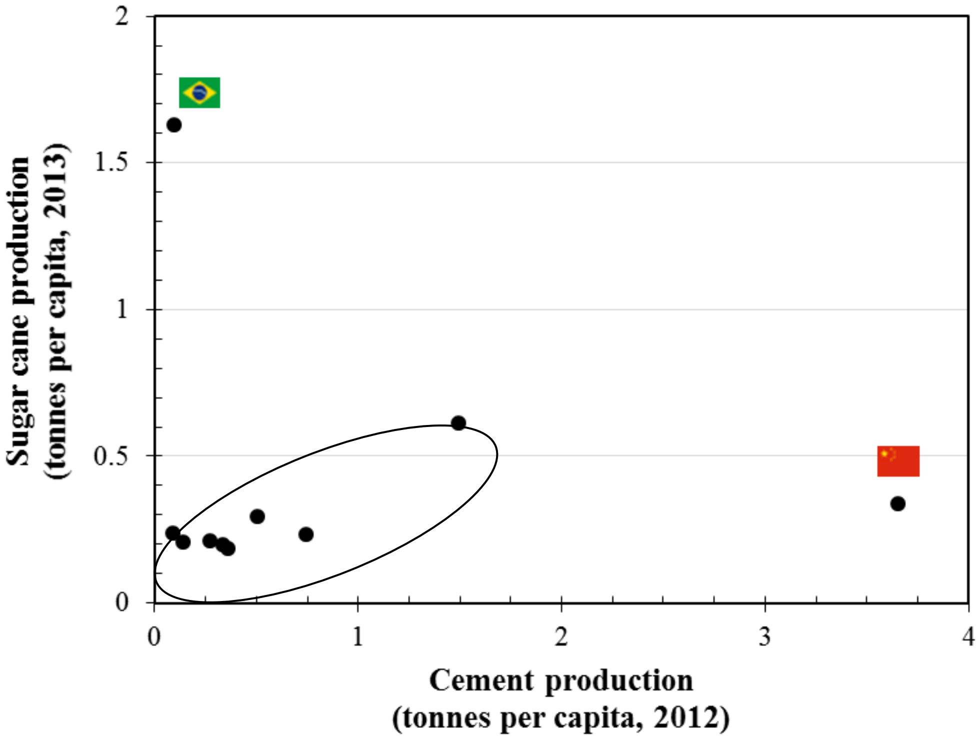

Figure 7. Comparison of sugar cane and cement production per capita (top 10 global sugar cane producers). Data from [130–132]

It has been reported[133] that for every 10 tonnes of sugarcane crushed, a sugar factory produces nearly three tonnes of wet bagasse, which is thus a highly significant source of waste produced worldwide. Sugar cane bagasse is used for several applications, including in the production of animal feed, enzymes, amino acids, organic acids and compounds of pharmaceutical importance;[134] however, it is also often utilised as fuel in sugar cane mills. Bagasse combustion produces silica-rich ashes which have been studied over the past decades as supplementary cementitious materials.[135–139] In Brazil alone, the generation of sugar cane bagasse ash (SCBA) is equivalent to about 6% of national Portland cement production,[140] which could potentially mitigate more than 500 kilotonnes of CO_2 emissions per year if the SCBA were to be used as a partial cement replacement.

A limited number of studies have been carried out to demonstrate the utilisation of sugar cane bagasse ashes as precursors for alkali-activated cements. Castaldelli et al.[141] demonstrated that it is possible to produce alkali-activated cements based on a blend of blast furnace slag and SCBA, with compressive strengths of up to 60 MPa after 55 days of curing at 20 °C, and low porosity. In a later study, the same group[142] also produced cements from alkali-activated fly ash blended with sugar cane bagasse ash which had been thermally treated to reduce its content of organics. These cements developed good compressive strengths when cured at 65 °C, associated with the formation of an aluminosilicate type gel as the main reaction product.

More recently Pereira et al.[143] also produced blended activated cements based on blast furnace slag and SCBA, and evaluated the durability of these binders when exposed to hydrochloric acid, acetic acid, ammonium chloride, sodium sulfate and magnesium sulfate. These cements performed much better than Portland cements when exposed to ammonium chloride, acetic acid and sodium sulfate; however, little advantage was observed when the specimens were exposed to hydrochloric acid or magnesium sulfate. The partial substitution of slag by sugar cane bagasse ash did not have a significant effect in the phase assemblage or mechanical strength development of the assessed cements. Therefore, it was proposed that this might be a feasible way to reduce the production cost of alkali-activated blast furnace slag cements by achieving good performance with lower contents of this more expensive precursor, and also to maximise the re-use of sugar cane bagasse ashes, particularly where exposure of the hardened material to certain chemically aggressive conditions is likely.

4 Wastes from the mining and mineral industries

4.1 Red mud

Red mud is an alkaline waste with a pH between 9.2 to 12.8 in the untreated state,[144] generated from alumina extraction via the Bayer process, where the bauxite ore is treated with sodium hydroxide solutions. When most of the aluminium has been extracted from the ore, the red mud has a high quantity of entrained NaOH, and contains iron oxides that give its red colour. This waste can contain high contents of silicon, as well as some residual aluminium whose quantity depends on the efficiency of the Bayer process operations, often present as zeolites or related aluminosilicate mineral phases. The worldwide annual generation of red mud is estimated at 120 million tonnes/year, which makes its disposal an issue of great environmental importance.[145]

The development of mechanical strength through alkali-activation of red mud is limited by the low available aluminium content of most of the red mud sources which have been tested. However, the use of a more aluminium-rich red mud,[146] or adding metakaolin[147] or fly ash[148,149] as secondary sources of aluminium, can contribute to improve the mechanical strength development of the alkali-activated binder. Kumar et al.[150] have produced paving blocks based on alkali-activated fly ash/red mud blended cements which comply with the relevant Indian national legislation (BIS IS 15658:2006) for precast concrete blocks, and with low leachability of alkalis. Alkali-activated blast furnace slag/red mud blended binders have also been developed,[151–153] and the slag significantly increased the compressive strength of these materials.

Ye et al.[153,154] identified that thermal treatment of red mud increases its reactivity in alkali-activation; however, it was still not sufficiently reactive to develop a measurable compressive strength when simply mixing the calcined red mud with water, despite its high initial alkalinity. In a following study, Ke et al.[155] added NaOH prior to the thermal treatment of the red mud, which favoured the formation of hydraulic phases including a disordered peralkaline Na-aluminosilicate, tricalcium aluminate and α-dicalcium silicate. This modified red mud reacted with water, without requiring the addition of an additional alkali-activator, and hardened monoliths with a measurable compressive strength were produced. This study demonstrated that utilisation of red mud for producing just 'added water' alkali-activated cements is feasible via alkali-thermal activation, although the cost-effectiveness of such a process requires further investigation and a secondary source of inexpensive alkalis.

4.2 Kaolin wastes

Kaolin is one of the most important clay minerals exploited for the manufacture of paper (~45%), ceramics (~15%), refractories (~15%), and other products. The United States, Uzbekistan, Czech Republic, Germany and Republic of Korea are the largest producers of kaolin, with an annual total production estimated at ~23 millions of metric tons.[156] The clay is often extracted from open-cut mines and is processed by different treatments (thermal, mechanical or chemical) to remove impurities, enhance whiteness, and/or adjust particle size distributions and shape. Wet processing is widely used to produce kaolin products for the paper industry and in filler applications. In this process, a dispersed kaolin-water suspension is passed through screens, hydroseparators, or hydrocyclones to remove the coarser mineral particles. Thereafter, whitening to increase brightness is carried out. The rejected kaolin sludge is now generating a considerable environmental impact due to the large areas required for its disposal.[157,158] This mineral waste is formed mainly of coarse kaolinite particles and some traces of quartz and/or anatase.[159]

In recent years, the mining industry has become motivated to find a suitable application for the rejected kaolin sludge, with a view towards its potential valorisation. In this sense, dried kaolin waste has been assessed as an aggregate in asphalt concrete.[160]

The controlled thermal treatment of kaolin sludge at temperatures around 700 °C transforms the waste kaolinite into metakaolin, which is a material with higher added value. This metakaolin derived from calcined kaolin sludge (CKS) exhibits pozzolanic properties and high reactivity in cementitious systems[161,162] and in zeolite synthesis.[163,164]

This reactivity indicates that CKS is potentially suitable for use in the production of alkali-activated binders. Longhi et al.[165,166] assessed the use of a Brazilian kaolin waste, which was thermally treated at 700 ºC and ball milled, then activated with sodium silicate solution. The resulting geopolymers exhibited high mechanical performance (up to 70 MPa in compression), comparable to the strengths achieved through the use of a much more expensive commercial metakaolin as precursor, and the coarser particle size of the CKS is actually to some extent beneficial in improving the fresh-state properties of the geopolymer mixes. Alkali-activation thus appears to be a technological and feasible solution for the valorisation of this industrial waste.

4.3 Low purity clays

The search for low cost or easily available materials for production of alkali-activated cements has led to the assessment of ‘normal clays’ such as montmorillonites, smectites and illites, among others. These clays are widely available all over the world, and may show reactivity with alkalis after thermal activation.[167–169] However, they tend to be more variable in composition and mineralogy than commercial kaolinites, and the parameters of the thermal activation process must be particularly precisely controlled in order to reach high reactivity.[170] So, extensive research is required to elucidate the factors that control the performance and long term stability of alkali-activated cements based on normal clays.

Two particular types of clays, bentonite and lateritic soils, are the object of alkali-activation research in several countries. Laterites are soil types rich in iron and aluminium, formed in hot and wet tropical areas, and contain kaolinite in which a high proportion of Al^{3+} is replaced by Fe^{2+} or Fe^{3+}.[171] When thermally treated between 750 °C and 800 °C, the kaolinite and gibbsite present in the soil transform into metakaolin and amorphous alumina,[172] which show pozzolanic activity and can be used as supplementary cementitious materials for concrete production.[173] In recent years, there has been a growing interest producing alkali-activated cements based on calcined lateritic soils. Silva-Neto et al.[174] and Gomes et al.[175] have demonstrated that Brazilian laterites are suitable precursors for alkali-activated cement production. In these systems the iron is seen to play a significant role in the development of the binding phases, so that iron distribution in the aluminosilicate type gels appears to occur via formation of Fe-Al-Si oxide amorphous structures. Although the structural role of Fe^{3+} as a substituent for Al^{3+} in these aluminosilicate gels remains poorly understood, screening methodologies such as those presented by McIntosh et al.[176] for the Fe-rich kaolinite resources of Northern Ireland offer the possibility to identify and exploit these lower-purity clay deposits, which would otherwise be of little or no economic value, as precursors for alkali-activation. The potassium silicate-activated mixes described in that study reached strengths as high as 89 MPa at 7 days.

Lassinantti-Gualtieri et al.[177] assessed the effectiveness of either acidic (phosphoric acid) or basic (sodium silicate) activation of laterite soils, before and after thermal treatment, to produce alkali-activated cements. It was demonstrated that thermal treatment of the laterite is required prior to chemical activation, and that both pathways of activation could promote the formation of hardened solid binders from a suitably calcined precursor. The acid phosphate chemistry described in this context appears in some way similar to the ‘Ceramicrete’ phosphate-bonded ceramics, and also to published work based on the combination of phosphoric acid and pure metakaolin,[178] but the cost of phosphoric acid is rather high and so is likely to restrict its use in large-scale applications.

Bentonite is a montmorillonite type clay that can be thermally treated to produce a pozzolan, and can be used by the construction industry as a supplementary cementitious material.[179,180] There exist a limited number of studies related to alkali-activation of thermally treated bentonite. Hu et al.[181] carried out a study using non-treated bentonite as an additive (less than 15 wt.%) in alkali-activated fly ash binders, identifying that this clay acted as a filler and contributed to densify these binders. Chervonnyi et al.[182] utilised alkali-activated thermally treated bentonite for the solidification of low-level radioactive ashes from the Chernobyl accident region. Monoliths achieved 12 MPa after 28 days of curing, and showed significantly lower leachability of strontium compared with Portland cement grouts. This suggested that alkali-activated cements based on bentonites could be an environmentally beneficial process for treatment of radioactive wastes.

More recently García-Lodeiro et al.[183] evaluated thermally treated bentonites as the sole precursor for producing alkali-activated cements. This study elucidated that effectively alkali-activated thermally treated bentonites produce hardened solids, whose strength is dependent on the availability of Si and Al in the system. The addition of highly soluble sources of Al, such as sodium aluminate, improved the compressive strength of these binders.

The alkali-activation of low cost normal clays such as bentonites and laterites, which are highly available in growing countries where the need for infrastructure is pressing and will increase in coming years, seems a viable alternative pathway to produce affordable construction materials.

4.4 Other mining and mineral wastes

Mining wastes are fine and coarse mineral materials resulting from mining and mineral processes operations, which usually are collected, transported and placed in large heaps or dams.[184] Approximately seven billion tons of tailings are produced worldwide each year, much of which consists of clay-rich minerals which are impure and considered to be of low value, but which may offer significant value as precursors for alkali-activation, particularly in applications such as mine backfilling where the ability to replace Portland cement offers the possibility to reduce costs and gain environmental benefit.[185]

One such source of low purity clays from the mining industry is a tungsten mine waste from Portugal, which is an aluminosilicate rich in clay minerals and iron. When thermally treated at 950 °C, dehydroxylation and amorphisation of this waste has been identified,[186] consistent with its significant content of phyllosilicate clay minerals. Pacheco-Torgal et al.[187] evaluated the effect of NaOH and $Ca(OH)_2$ concentrations on the mechanical performance of alkali-activated calcined tizatugsten mine waste, and used these results to develop a material with an optimised activator content,[186] as well as lower shrinkage than Portland cement and low water penetration. Conversely, the blending of sodium carbonate with the tungsten mine waste hindered the dehydroxylation of the waste, and even though a high compressive strength was achieved at early times of curing, a reduction in the stability of these cements was observed when immersed in water.[188]

Other mining wastes that have been utilised to produce alkali-activated cements include those obtained from copper mining, which are rich in feldspars and can be used in the production of bricks;[189,190] heavy metals are also able to be effectively immobilised in these materials.[191] The addition of a small quantity of sodium aluminate can enhance the strength development of these materials, depending on the temperature of curing,[190] which suggests that the availability of aluminium from the mining wastes was limiting the performance achieved. For this reason, the combination of copper mine wastes or tailings with other aluminous materials has also been identified as advantageous in alkali-activation; Zhang et al.[192] produced copper mine tailings/fly ash-based alkali-activated cements, where fly ash addition promoted high compressive strengths and relatively rapid strength development. Ahmari et al.[193] produced alkali-activated cements by blending copper mine tailings with low-calcium flash-furnace copper smelter slag and an alkali activator. The addition of the smelter slag enhanced the mechanical strength and promoted the formation of a denser microstructure, as a consequence of the high solubility of silica from the slag and its fine particle size distribution. However, elevated temperature curing was required to accelerate the hardening of the specimens. Ren et al.[194] also showed that aluminium sludge could be effective as a secondary source of Al_2O_3 in an alkali-activated blend with copper mine tailings, to decrease the overall Si/Al molar ratio and improve the performance of the resulting binders.

Caballero et al.[195] utilised a silica-rich gold mining waste, derived from the grinding and subsequent separation of sulfides from quartzo-feldspathic gneiss, as the main precursor to produce alkali-activated cements, with minor Portland cement addition to accelerate early reaction. These cements developed compressive strengths of up to 45 MPa, and presented a high resistance to when exposed to sulphuric acid, but degradation of the specimens was identified upon exposure to nitric acid. In both sodium and magnesium sulfate solutions, these cements gained strength at extended times of immersion. In another study, the alkali-activation of thermally treated halloysite blended with volcanic glass and gold extraction tails was reported by Barrie et al.[196] The cements thus produced developed good compressive strength (30 MPa), and immobilisation of zinc and lead present in the tails was achieved in these alkali-activated cements. However, high leachability of arsenic and copper was identified in these specimens, which makes the material unsuitable for construction purposes, and so it was suggested that these activated cements may be most effectively used for back-fill purposes or as capping materials.[196]

5 Wastes from other industries

5.1 Coal bottom ashes

Coal is the most abundant fossil fuel used for electricity generation, and its relatively low cost and large deposits represent a reliable source of energy. Around 7.1 billion of tonnes of coal is used worldwide every year.[197] The main coal combustion wastes (or by-products) are fly ash, bottom ash, flue-gas desulfurisation products, and boiler slag. These wastes are mainly used as raw materials for the construction industry in the production of clinker or blended cements and concretes, in civil engineering (as subgrade stabilisation, pavement base course, and structural fill), and for site restoration in open cast mining.[198,199] However, the majority of these materials are eventually sent to landfill rather than being effectively re-used.

Coal fly ash (FA) is currently playing an important role in the concrete and cement market due to its low cost and pozzolanic reactivity,[200] and has been discussed in the context of its use in alkali-activation in several major reviews, so will not be the focus of discussion here. The second most important residue generated during coal combustion is coal bottom ash (CBA), which represents up to the 20% of the total ash generated. The CBA is collected at the bottom of the furnace and consists of larger, granular and glassy heavier particles. The total production of CBA in the European Union (EU15) is estimated to be ~4.1 Mt per annum, and only 46% of this is re-used efficiently.[201] In the U.S., the total production of CBA reported in 2012 was 14.1 Mt with a utilisation rate of 38.8%.[202]

Although FA and CBA have similar origins, their physical and chemical features differ widely. In particular, the CBA generally contains more heavy metals than the fly ash. Therefore, in some countries, the most recent regulations and policies for the safe disposal of coal combustion wastes have modified the management of CBA.[203] Taking into account the large volume that is disposed in landfill, CBA is becoming an environmental and economical concern due to the large land areas used, as well as the ground and water contamination by leaching of trace elements. CBA has been used as an artificial aggregate in concrete by substitution for sand,[204,205] and also shows some pozzolanic reactivity, which can be improved through mechanical treatment.[206,207] However, its use as a supplementary cementitious material has not been widely accepted due to its high porosity and low density, which have a negative effect on water demand.[207]

A significant alternative route for the valorisation of CBA is its potential use as a raw material for the production of alkali-activated cements, as a consequence of its relatively high content of SiO_2 and Al_2O_3 in reactive form.

However, Chindaprasirt et al.[208] provided a comparative assessment of alkali-activated binders produced with FA or CBA (both with CaO contents of ~16.5%), and found that the compressive strength achieved by the FA-based binders was considerably higher than was achieved with the CBA, due to the higher reactivity and higher content of amorphous phases present in the FA. As was noted above related to the utilisation of CBA as a pozzolan, the application of mechanical treatment can also increase its reactivity in alkali-activation, and thus mortars with improved mechanical performance and higher workability can be obtained.[209] The differences in chemical composition, degree of amorphicity and particle size distribution of the diverse CBAs generated in different thermoelectric plants lead to an intrinsically high variability in the development and optimisation of alkali-activated binder formulations based on these materials.

Because the development of CBA-based alkali-activated binders has increased only recently, there exist few reports related to the performance of these materials when exposed to aggressive environments. Sata et al.[210] studied alkali-activated binders derived from a milled CBA exposed to 3% H_2SO_4 and 5% Na_2SO_4 solutions. The mortars exhibited excellent performance after immersion in these sulfate solutions, which is even better when finer CBA is used due to the finer pore size distribution and consequent lower permeability of the binders.[211]

As an alternative method to using alkali-activation directly to convert waste into cementitious binders, Geetha and Ramamurthy[212] reported the effectiveness of a pelletisation method for the production of artificial coarse aggregates through the alkali-activation of CBA using blends of NaOH, sodium silicate and $Ca(OH)_2$. Although their results elucidate a novel potential route to valorisation and application of CBA, further assessment is required in order to understand the performance of these synthetic aggregates in concrete mixes, as well as the economic and environmental feasibility of their production through the alkali activation of CBA.

In general, the volume of CBA generated worldwide is continuing to increase as the worldwide demand for energy grows, and the development of new methods for the safe disposal or valorisation of this material is essential. Its chemical and physical properties are more challenging, and more variable, than those of the fly ash which results from the same coal combustion processes, but this also means that the competition from other potential users of CBA is much lower and so it offers significant potential for development in future years.

5.2 Paper sludge ash

It has been estimated that one tonne of paper sludge is generated per three tonnes of paper produced,[213] and considering the total worldwide annual production of 403 million tonnes of paper,[214] this means that more than 130 million tonnes of paper sludge need to be valorised or disposed worldwide each year. Some of the strategies adopted for the management of paper industry wastes include incineration with energy recovery, pyrolysis, steam reforming, production of mineral fillers for building materials such as cement, among others.[213] In particular, paper sludge ash is a by-product derived from the incineration of paper sludge, which can contain varying quantities of thermally-amorphised clays and partially decomposed calcium carbonate, depending on the proportions of clay and calcite used in paper production. The potential use of this ash as a supplementary cementitious material has been studied over the past decade,[215,216] considering the importance of both calcined clays and limestone as mineral admixtures for Portland cement.

A limited number of studies have been carried out using paper sludge ashes as a precursor for alkali-activated cements. In preliminary work, Yan et al.[217] identified that the partial substitution of fly ash with dried (uncalcined) paper sludge reduced the workability and compressive strength of the alkali-activated cements; however, it did promote a refinement of the pore structure which led to a reduced drying shrinkage of the material. Antunes Boca Santa et al.[218] produced alkali-activated calcined paper sludge cements blended with coal bottom ashes, as the calcined paper sludge utilised was partially crystalline and not highly reactive. Higher contents of bottom ash contributed to increase the mechanical strength and density of the cements.

More recently, Gluth et al.[219] reported higher compressive strengths in water-hydrated paper sludge ash paste compared to the same ash activated by NaOH or KOH, after 28 days of curing. All of the portlandite formed by hydration of the free lime in the ash was consumed during the first 7 days of curing. Bernal et al.[220] utilised a paper sludge ash rich in free lime as a precursor for production of alkali-activated cements. This particular paper sludge ash was highly reactive, and when combined with either water or an alkaline solution, it formed hydrated reaction products including AFm-type phases, portlandite and a highly disordered C-A-S-H type phase. The inclusion of an alkaline solution (either sodium hydroxide or silicate) increased the dissolution rate of free lime, and consequently favoured the formation of more Ca-rich phases compared to the water-hydrated paper sludge ash.

Considering the significant differences in composition, particularly the content of free lime, between paper sludge ashes from different sources, it cannot be stated that this waste will generically be suitable for production of alkali-activated cements, as the activation reaction will proceed in a different way depending on the content of calcium present in the ash. However, with the correct combination of ash, activator and secondary (likely siliceous) precursors, it does appear possible to produce good-quality alkali-activated materials from paper sludge ash, and this would seem to be a high value-added end usage for these ashes.

5.3 Spent fluid catalytic cracking catalyst

Fluid catalytic cracking catalyst (Figure 8) is an aluminosilicate product, often based on a zeolitic framework, used extensively in oil refineries. Once this catalyst loses its activity (becomes ‘spent’), and if it cannot be effectively or economically regenerated, it is discarded and treated as waste. This waste catalyst has been studied as a potential supplementary cementitious material for the production of blended cements,[221,222] and high performance mortars and concretes have been produced in this manner. The reactivity of this waste varies depending on the nature of the initial catalyst used,[221,223] therefore optimisation studies are required when using materials from different sources. The production of this waste is relatively low, around 800,000 tons per year worldwide in 2010,[224] which has limited its large-scale adoption as a partial replacement of Portland cements in concrete production.

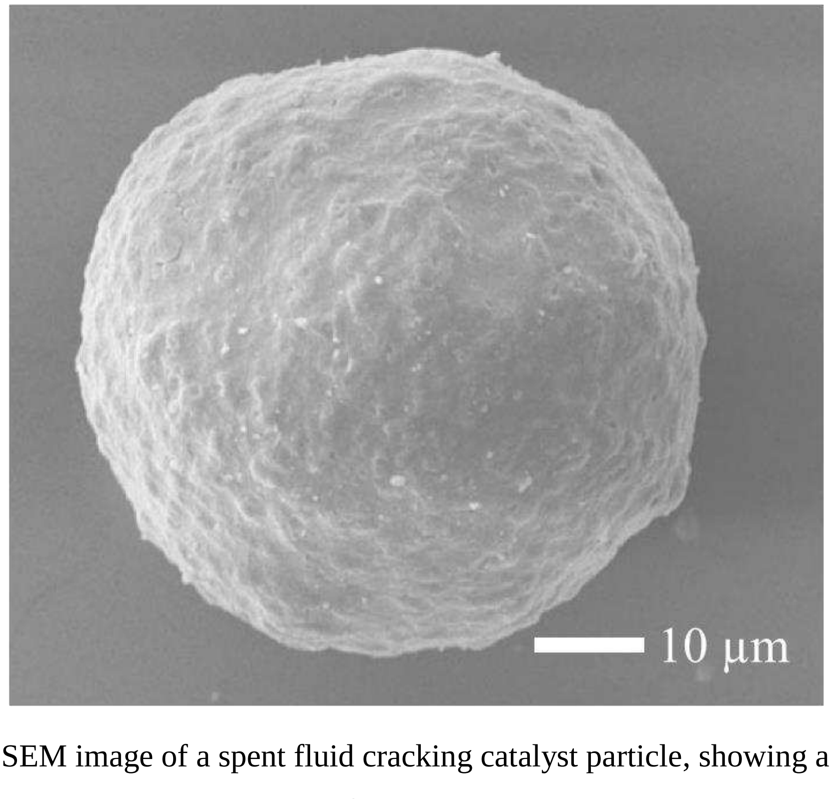

Figure 8. SEM image of a spent fluid cracking catalyst particle, showing a spherical particle morphology and absence of micron-scale pores, as well as bright regions which are likely to correspond to high local concentrations of heavy metals. From Bare et al.,[225] copyright John Wiley & Sons.

In recent years, Tashima et al.,[226,227] Rodríguez et al.[228] and Trochez et al.[229] utilised fluid catalytic cracking catalyst residues as sole precursors for producing alkali activated cements. These studies have been focused on evaluating the effects of different formulation parameters on the microstructural development of these materials, their phase assemblage and compressive strength. There is a good consensus that this waste is a suitable precursor for producing alkali-activated cements, which can develop a high compressive strength depending on the formulation adopted for its production. In the case of Tashima et al.[226,227] high temperature curing (65 °C) was utilised, while Rodríguez et al.[228] and Trochez et al.[229] cured their samples at 40 °C and 25 °C, respectively, and the materials obtained developed compressive strengths comparable to those reported for high temperature cured specimens. Significant differences in the nature of the alkali activation reaction products between sources of spent fluid catalytic cracking catalyst waste have been identified across these studies, and therefore it is necessary to identify the characteristics of the waste, particularly mineralogy and particle size distribution, that control its performance when used as a precursor for alkali-activated cements.

The alkali-activation of this waste might be of interest for its treatment or valorisation, depending on the content of toxic and hazardous elements present, as both catalytic heavy metals and contaminants deposited on the catalyst in use can be important in determining the availability of hazardous species from the waste catalysts. Further investigation of these systems is required to elucidate whether these cements can develop specialised technical properties to make their development sufficiently attractive for commercial purposes.

6 Summary and general considerations

Table 1 provides a summary of the nature and production of the wastes discussed in this review, and their characteristics which are particularly relevant to use in the production of alkali-activated cements and concretes.

Table 1. Summary of wastes considered, and key factors defining their utilisation in alkali-activated cement materials.

	Quantities available	Use in alkali activation technology	Disadvantages if used in alkali-activation	Potential advantages for use in alkali-activation	Waste classification[230]
Ashes from municipal waste incineration	EU-27 incinerates ~58 Mt of MSW (2012), producing between 6-18 Mt of BA.[231] The main cities in China generated more than 172 Mt in 2014.[232] The US generated 254 Mt of MSW in 2013, where 13% (~33 Mt) was incinerated and ~8 Mt of BA was produced.[15]	As precursor. As a secondary precursor As aggregate	- Presence of toxic compounds including: metal chlorides, metal sulfates, metal carbonates, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, chlorobenzenes, chlorophenols, chlorinated compounds, benzofurans and heavy metals. - Lower reactivity when compared to traditional precursors. - High heterogeneity in chemical and physical properties among batches. - High water demand due to its high porosity and specific surface area. - A decontamination process could be necessary. - Absence of policies for its re-use in other production processes. - Most of the alkali-activated products will likely require thermal curing - The production of materials with high mechanical performance is limited.	- Reduction of harmful substances released to the environment due to their encapsulation. - High interest to find alternative routes for disposal.	19.01.11/19.01.12: Mirror hazardous / Mirror non-hazardous
Ceramic and demolition wastes	- Construction and demolition waste: - EU-27 generates ~860 Mt. - China generates ~2.19 Gt.[233] - Demolition wastes are not rigorously tracked in U.S. However, the amount estimated in 2012 was approximately 480 Mt.[234] - Ceramic waste: - Ceramic tile production climbed to 11.913 billion square metres with growth overwhelmingly confined to Asia and non-EU Europe.[61] - China, Spain and Italy are the three largest exporter countries, accounting for 66% of world exports. - China, Brazil and India remain the top three tile producer and consumer countries. - The ceramic tile industry generates a large volume of ceramic waste outputs to landfill estimated at 85_kt in 2007 from both excess stock and defective products. [235]	As precursor As a secondary precursor As aggregate	Construction and demolition waste: - High heterogeneity in chemical and physical properties. - Requirement of a classification process due to the presence of different materials (wood, plastic, glass, metal, etc), as well as a milling treatment. - Low reactivity when compared to other precursors. - The alkali-activated products will likely require thermal curing. Ceramic waste: - Low reactivity when compared to other precursors.	Construction and demolition waste: - High interest to find alternative routes for disposal. Ceramic waste: - Better homogeneity in chemical and physical properties when compared to demolition wastes	- 17.01/17.01.07: Mirror non-hazardous
Wastes or sediments from water plants	According to the FAO/AQUASTAT database,[236] the values reported between 2008-2015 for municipal waste water production are: Africa: 12.47 Gt/y; Americas: 94.27 Gt/y; Asia: 123.46 Gt/y; EU: 35.54 Gt/y. The estimated sewage sludge production rates in dry metric tons per annum are: EU-27: 8909 (2010); US: 6514 (2004), and China: 2966 (2006).[237]	As a secondary precursor Immobilisation	- Limited availability of sewage sludge. - Low reactivity due to its low content of amorphous aluminosilicate compounds. - Requires the use of a primary aluminosilicate precursor with high reactivity. - Presence of heavy metals (including Zn, Pb, Cd, Cu, Hg, Zn, and Ni). - Depending on its mineral composition a thermal process could be required (particularly for clay-rich sediment sludges). - Waste water treatment capacity is strongly related to national development. - Absence of policies for its re-use in other production processes. - The alkali-activated products will likely require thermal curing - The production of materials with high mechanical performance is limited.	Reduction of harmful substances released to the environment due to their encapsulation.	9.02.06/19.08.12: Mirror hazardous/ Mirror non-hazardous
Waste glass	EU-28 glass production 20.85 Mt with a recycling rate of 71% (2013).[238] In U.S. the glass container generation and recovery in 2012 were 11.57 Mt and 3.2 Mt, respectively.[239]	As a source of SiO_2 for the production of the alkali activator	- Limited availability of the residue. - Requirement for a classification process - Presence of high content of Hg when the waste contains used fluorescent lamps. - Low volumes of waste can be valorised due to the low amount of extra SiO_2 required during alkali activation. - Chemical dissolution of amorphous phases can be required.	- There exist targets to achieve higher reuse rate - Reduction of cost of binder production due to the substitution of waterglass, which is the component with the highest price. - Improved performance of alkali-activated systems when used as a soluble source of SiO_2.	15.01.07/19.12.05/ 20.01.02: Absolute non-hazardous 17.02.02: Mirror-non hazardous
Rice husk ash	In 2014 the global production of paddy rice was 746 million metric tonnes. [100] Assuming that 20% of paddy rice is husk, ~150 Mt of this residue was generated. When the husk is burned, 25% of ashes is generated, which represents ~38 Mt.	As a source of SiO_2 for the production of the alkali activator.	- Depending on the control of the thermal process, high contents of unburned material can be obtained. - Other potential applications are available, which could increase cost. - The transport cost of the residue can be high due to its low density. - Activator solutions can exhibit a dark color, which might affect the aesthetics of the final product. - Requires an extra investment within the alkali-activation technology/process for its dissolution in order to obtain a high quality activator. - Lower volume utilisation when compared to materials used as precursors, due to the low requirements for soluble silicates during the activation.	- Reduction of cost of binder production due to the substitution of waterglass solution, which is the component with the highest price. - Alkali activator with a specific M_2O/SiO_2 ratio can be produced. - When produced under optimal conditions, similar performance can be achieved compared to commercial soluble silicate solutions. - Activator solutions with other alkaline cations can be also produced. - High number of reports elucidate its feasibility for use in activator production.	Not specified in this standard.
Palm oil fuel ash	The global palm oil production for 2015 was 62.6 Mt.[240] Assuming that ash equivalent to 10% of this mass is generated, approximately 6.3 Mt of waste is obtained.	As precursor As a secondary precursor	- Low content of reactive alumina. - Most of the systems likely will require thermal curing - Few reports related to its performance and effectiveness as a precursor. More studies are required.	- The presence of calcium (5-15%) can improve its performance as precursor.	Not specified in this standard.
Sugar cane bagasse ash	Brazil is the world's largest sugar cane producer (around 650 Mt in 2013), which corresponds to 30% of the world's production.[129] Brazilian sugarcane industry generates a considerable amount of sugarcane bagasse ash, estimated at about 2.5 Mt/y (Cordeiro, 2006).	As a secondary precursor	- The content of Al_2O_3 is not sufficient to be used as a main precursor.	- High production in markets with high demand for construction materials.	Not specified in this standard.
Red mud	120 Mt/y of red mud is generated[241] and currently a quantity in storage of more than 2.7 Bt is estimated.[144]	As precursor As a secondary precursor	- High content of Fe_2O_3, whose participation during the alkali-activation technology and mechanical performance improvement is not well understood (may be positive or negative). - According to the efficiency and effectiveness of the Bayer process, the content of reactive Al_2O_3 can be extremely low.	- After thermal treatment the red mud can be considered a good alternative to produce one-part alkali-activated systems (just adding water).[155] - Alkaline residue (mainly with high contents of dissolved NaOH).	01.03.09: Mirror non-hazardous
Kaolin wastes	The United States, Uzbekistan, Czech Republic, Germany and Republic of Korea are the largest producers of kaolin, with an annual total production estimated at 23 million metric tonnes.[156] The Brazilian mining industry generates ~0.5 Mt/y of kaolin sludge waste, with a stockpile of ~10 Mt.[242]	As precursor	- Requires thermal treatment to increase its reactivity - Particle shape reduces the workability of the fresh mixtures - Reactivity degree is dependent on the kaolinite content. - Kaolin sludge can be re-used for other industries and applications.	- Materials with high mechanical performance can be obtained (even comparable to pure MK-based systems). - Depending on the source, the chemical and mineralogical composition might be homogeneous.	Not specified in this standard.
Coal bottom ashes	In 2010 the global production of coal combustion products (CCP) was estimated at 780 Mt. Considering that the ~15% of the overall CCP is CBA, the generated estimated value is around 117 Mt.[8] Annual production quantities of bottom ash in US and EU were about 14 (American Coal Ash Association (ACAA), 2014) and 4 (European Coal Combustion Products Association (ECOBA), 2012) million tonnes in the last decade, respectively.[243]	As precursor As a secondary precursor	- Low reactivity. - High heterogeneity in chemical and physical properties among batches. - The production of materials with high mechanical performance is limited. - The alkali-activated products will likely require thermal curing -	- High interest to find alternative routes for disposal.	10.01.01: Absolute non-hazardous

	Coal fired thermal plants in India produce about 131 million tons of coal ash, which comprises about 25 million tons of coal bottom ash[204]				
Paper sludge ash	Production of 125 kt per annum in the UK.[244] Confederation of European Paper Industries (CEPI, 2014) states that pulp and paper industry landfill disposal has declined by 55% over the last 12 years, from 32.7 to 14.3 kg/tonne of product.[245]	As precursor As a secondary precursor	- Requires thermal treatment in order to increase its reactivity. - Particle shape may reduce the workability of the fresh mixtures - Reactivity is dependent on the kaolinite content.	- Thermal treatment conditions for this material are similar to those used for pure kaolinite - Optimisation considers the decomposition of organic material and the prevention of free lime formation from calcite.	03.03.02: Absolute non-hazardous
Spent fluid catalytic cracking catalyst	The global production is estimated at ~200 kt/y.[246]	As precursor	- Low production when compared to the other residues. - The residue requires and previous treatment in order to reduce the content of harmful elements, including V, La, and others.	- High reactivity - Homogeneity in its chemical composition among different batches. - The waste is constituted mainly of SiO_2 and Al_2O_3. - Materials (mainly mortars) with high mechanical performance can be produced.	16.08.04: Mirror non-hazardous

One additional key consideration, which is relevant across many of the wastes discussed in this review, is organic carbon content. The content of organic carbon, particularly when present as unburned material in wastes generated via thermal processes, must be considered carefully in the design of alkali-activated cements. The presence of a high content of porous and non-reactive organic particles, with a high specific surface area, significantly increases the water demand of the fresh mixtures with a consequent negative effect on the rheological and mechanical properties of the material. These particles can also absorb the activator solution, which reduce the alkali concentration during the reaction process. Fernandez-Jiménez and Palomo suggested that a suitable coal FA must have loss on ignition values lower than 5%.[247] However, there exist studies related to the production of alkali-activated materials using different industrial wastes or by-products derived from thermal processes with higher contents of organic matter, including coal fly ash,[248–251] coal bottom ash,[212,252–255] municipal solid waste ashes,[256,257] palm oil fuel ash,[120,122,128] and sugar cane bagasse ash.[141] Taking into account that the high content of un-reacted material reduces the effectiveness and reactivity of these wastes as precursors, blending with another more-reactive aluminosilicate may be required. When the mechanical performance requirements for the material are higher, the use of precursors with a high content of unburned material can be restricted.

One of the methods which is often used to reduce the organic carbon content of waste ashes is a more extended (or higher temperature) combustion process, which consumes the carbon, but often at the cost of inducing partial crystallisation of the silicate or aluminosilicate phases and thus reducing their reactivity. A balance is therefore required between carbon elimination and reactivity retention, which necessitates careful process control and parametric optimisation to achieve the best results when producing alkali-activated cements using siliceous wastes.

Additionally, as discussed in section 3, it is very unlikely that pure siliceous wastes would be suitable for use as a sole precursor in alkali-activation due to their low Al content; blending with an aluminous material will always be necessary. For these reasons, the Si-rich wastes including SCBA, RHA and glass waste have generally been used as a source of amorphous silica for the alkaline activator. Although some of the residues included in this review have been chemically modified in order to be used as alternative alkali activators, the open literature also reports the use of other industrial wastes that are suitable for potential re-use as waste derived activators. A sodium aluminate and NaOH-based solution from the aluminium anodising process has been successfully incorporated as an activator in fly ash / blast furnace slag blends. Even though the time of setting of these alkali-activated systems were considerably longer, these materials were able to generate a 28-day compressive strength higher than 80 MPa.[258,259] This work, along with other reports of aluminate activation in fly ash-based alkali-activated binder systems,[260,261] offers yet another opportunity for the valorisation of problematic wastes in the production of this class of construction materials.

7 Concluding remarks

This paper has summarised the most important research findings related to different wastes that could be used for the synthesis of alkali-activated binders. Valorisation of a wide variety of metallurgical, societal and agricultural wastes can be achieved through the use of these materials as precursors or alternative sources of SiO_2 in the activator for alkali-activated binders and concretes. Most alkali-activated mixes are currently based on ground granulated blast furnace slag or on fly ash, with alternative wastes generally used in lower volumes. Blending of specific wastes in defined combinations, often involving one of these better-understood materials in conjunction with another alternative material, can offer a lower-risk and potentially highly attractive path to the utilisation of a broader range of wastes, as the quality control and metals leachability issues which are often associated with many of these materials are reduced through dilution.

Standardisation and large-scale commercial deployment of alkali-activation technology is taking place rapidly in many jurisdictions worldwide, and although most of the mixes now being used at production scale are based on a fairly narrow selection of precursors (coal fly ash, blast furnace slag, and calcined clays), a performance-based approach to standardisation does certainly offer scope for the utilisation and valorisation of a much wider range of silicate and aluminosilicate slags as precursors for the production of alkali-activated concretes.

In developing any new material or process for large-scale deployment, it is essential to ensure that there is a robust supply chain in place. This is particularly critical in the construction materials industry because of the enormous volumes which must be processed for an operation to be economically viable; a modern cement kiln has a throughput on the order of thousands of tonnes per day, whereas in most process industries this could easily represent the annual throughput of a large plant. The cement and concrete industry, the agriculture industry and the extractive metallurgy industry, are arguably the only process sectors which are equipped to handle a such a large volume of solids as both precursor and product, and this raises important questions when analysing a potential new route to market, or a new product. When defining whether a particular alkali-activated binder formulation will be worthy of commercial attention, the key question often becomes: is it possible to make enough of this material to become commercially viable? A large number of academic studies are conducted, and published, which describe the production of an alkali-activated binder system from particular combinations of industrial wastes and chemical feedstocks. However, if a particular waste material is available only in quantities of a few tens of tonnes per day, it will be very difficult to produce a commercially useful volume of alkali-activated concrete for general construction or infrastructure applications.

This means that the production of alkali-activated concretes based on waste streams of low to moderate volume will require some form of driver other than simply the production of a low-cost, standard-performance concrete to enable their use in a practical and profitable context. Specific environmental or cost benefits can arise from the use of a particular solid waste material (through diversion of materials from landfill) or source of waste alkalis (replacing some of the more costly sodium silicate activator) in large-scale alkali-activated concrete production), and sometimes the performance of alkali-activated materials derived from a specific lower-volume precursor can offer attractive opportunities for niche applications. Such properties include chemical and thermal resistance, and concretes displaying good performance in these areas can command a significant price premium over standard products. This is likely to be the area in which alkali-activation of waste materials will lead to commercially and technologically significant outcomes, and will enable the true valorisation of wastes from a wide range of industries and areas of society, as has been outlined in this review.

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