Durability in alkaline-activated materials
a review on the state of the art

Sebastião Ventura¹
Lino Maia²

¹ PhD Student, Faculty of Engeneering (FEUP), University of Porto, Rua Dr. Roberto Frias, 4200-465 PORTO, Portugal (up202101631@edu.fe.up.pt) ORCID 0000-0002-1524-3166
² CONSTRUCT-LABEST, Faculty of Engeneering (FEUP), University of Porto, Rua Dr. Roberto Frias, 4200-465 PORTO, Portugal (linomaia@fe.up.pt) ORCID 0000-0002-6371-0179

ABSTRACT: The present work on durability in materials obtained by alkaline activation (AAM), in state-of-the-art review format, is structured as follows. (I) -The concept of alkali activated materials-composition-performance; (II) - The prediction of the useful life of AAM-methodologies and planning; (III) - The durability and properties of Engineering-mechanical tests-standards of specifications and tests (IV) Degradation processes of Chemical Matrix-resistance to sulfates (SO₄²⁻), acids (HCl), (H₂SO₄) (HNO₃), (H₃PO₄), (HF), (H₂CO₃) and sea waters; (V) Degradation processes by mass transport - permeability, porosity, corrosion, carbonation, efflorescence and ice-thawed.

Keywords: Slags; Alkali Activation; Durability.

1-INTRODUCTION

The structure of this work is in accordance with the global vision of great concern about climate change, the use of concrete associated with world population growth, the production and consumption of ordinary Portland cement, previously regarded as (Ouellet-Plamondon, 2014) accounting for 5 to 8% of total anthropogenic CO₂ emissions, of which 95% of CO₂ is developed during cement production (Huntzinger DN and Eatmon TD, 2009), and most recently reported with a probability of reaching 10 to 15% of these emissions by 2020 (Worrell E, 2009). Such production has been contributing for decades to the degradation of the terrestrial platform through the exploitation of calcareous (CaCO₃) and clayey (Al₂O₃-2SiO₃-H₂O) materials; the increase in the production of carbon gel (CO₂) with the corresponding contamination of the atmosphere, thus increasing concern from the scientific and environmental community with the study and research of new alternative materials to ordinary Portland cement. Those alternative materials, considered supplementary cementitious materials, and their application in the field of engineering and civil construction have been studied with great focus on the concepts of construction durability, knowledge of - lifespan planning methodologies, analysis of applicable standardization, approach and determination of estimated lifespan in case studies as well as the implementation of measures that promote durability, and the studies of technical, environmental, socio-economic and financial impact on the partial or total use of slag from the incineration of municipal solid waste as a complementary cementitious material. These alternative technological improvements with new supplemental cementitious materials can be reliably expected to reduce CO₂ emissions by a factor of two (Habert et al., 2010), which will be far from the quadruple reduction target of the Intergovernmental Panel on Climate Change (IPCC) (United Nations...
Environment Programme 1988). This is due to the fact that these new materials are known to account for a lower level of carbon dioxide emissions than Portland cement. Worldwide, Portland cement production in the 1990s reached 1,200 million tons per year (Figure 1), having exceeded 2,600 million tons per year at the end of the 2000s with projections pointing to production above 5,200 million tons per year in 2050 (Taylor et al., 2006).

![Figure 1](image-url) - Forecast of global consumption of Portland Cement: Adapted from (Taylor et al., 2006; Pacheco-Torgal and Jalali, 2010).

The need to achieve carbon neutrality by 2050 has increased interest in alkaline-activated ligands - as a more environmentally friendly alternative to traditional Portland cement-based processes in the construction sector.

2-DURABILITY OF CONSTRUCTION

As for durability, according to van Deventer et al. (2011), the question of whether geopolymer concrete or AAMs are durable remains another important obstacle to broader commercial adoption. That means it is the question, not the answer, that continues to be the obstacle. Some would say that alkali-activated materials have undergone detailed research only recently and may not have decades of durability data to prove long-term stability, but this is not the case (Shi et al., 2006; Deja 2002). It can also be asked what evidence, in addition to structures that actively exist for long periods of time, current binding systems have to prove their fundamental durability. The answer is that there is very little - but the durability of Portland cement is not questioned, although recent analytical studies show significant changes in the nature of hydrated Portland cement binder and cement-slag mixtures over a 20-year period (Taylor, 2010).
Alkali-activated systems have the arduous task of proving themselves durable when the final measure, the presence of decades-old structures, is the only accepted verification tool. Most standard methods for testing the durability of cement and concrete involve exposing small samples to very extreme conditions – such as highly concentrated acid or saline solutions – for short periods of time. These results are used to predict how the material will fare under normal environmental conditions for - decades or more. (van Deventer et al., 2011). Predictive models depend on concepts that include mass transport through porous means, reaction kinetics, and particle packaging. When trying to prove durability, this approach is flawed insofar as it can only provide indications of expected performance under actual environmental conditions rather than any kind of definitive proof. In addition, the structure of the research community is fundamentally based around the time scale of graduate research projects, 3-6 years. This inherently leads to the problem that a "long-term" test is at least one order of magnitude smaller than the expected lifespan of most concrete structures. In those instances where projects are conducted for longer periods of time, there needs to be strong management and focus on the project, which is rarely seen. So the reality is that durability tests mean little in the absence of real-world validation (van Deventer et al., 2011).

The adoption of new scale materials is intrinsically very slow, as periods of 20 to 30 years are required to verify test results, and this is clearly not a time scale on which marketing efforts can be based. Therefore, there are two possible approaches, which are now being carried out in parallel: linking the durability of alkali-activated materials to the chemical structure using cutting-edge scientific techniques and putting into use as many real-world structures as possible with very well documented mixing projects as soon as possible, so that they can reach the required ages of decades or more, as soon as possible (van Deventer et al., 2011, p. 83).

Society is currently thinking about "Sustainable Development" in order to avoid quality problems in civil construction, and to take into account social, environmental and economic aspects, while encouraging the development of methods and tools to assess the durability of construction products, both traditional and innovative (Jernberg et. al., 1997). In this context, two complementary tools developed were 1-Data fusion procedure (left part of Figure 2) and 2-Analysis of Failure Modes and Effects (right part of Figure 2).

Figure 2 - Durability evaluation methods and tools (Lair et al., 2001)
3-ALKALI-ACTIVATED MATERIALS

As the main connecting material used in concrete production, ordinary Portland cement accounts for about 5% of the world's CO₂ generation (Provis and Bernal, 2014a), thus for economic and environmentally friendly reasons, it has been necessary to study other alternative building materials such as alkali-activated binders (van Deventer et al., 2010) (Provis, 2014c).

The pretreatment of Municipal Solid Waste Incineration Slag (MSWIS) has shown that its application reduces the content of chlorides, heavy materials and some organic material issues, and that washing with water is a common method for removing soluble salts such as NaCl, KCl or CaCl₂.

Wet grinding provides a basic environment for the dissolution of al-metallic aluminum in slag, and some comparative studies between the use of wet and dry grinding materials have shown that there is a greater performance in the compressive forces of mixtures containing wet grinding materials (VENTURA and MAIA, 2023, p. 19).

Alkaline-activated materials, also called "geopolymers", have been studied in recent decades as alternative binders to traditional Portland cement (Provis, 2014b). Alkali-activated systems have been studied since 1940, when Purdon observed the satisfying development of mechanical resistance in the activation of slags with alkaline solutions and lime (Pacheco-Torgal et al., 2008; Juenger, et al., 2011).

Glukhovsky (1994), who also devoted himself to the study of alkaline materials, noticed, in 1959, that these materials had a similar type of composition to that of many minerals and rocks that compose the Earth's crust. They were classified into two groups according to the content of the initial material: a) Me₂O-Al₂O₃-SiO₂-H₂O interpolymer or geopolymer system, and b) Alkaline-earth system Me₂O-MO-Al₂O₃-SiO₂-H₂O, where Me=Na,K... and M=Ca,Mg. System a) (Me₂O-Al₂O₃-SiO₂-H₂O) - refers to alkaline materials rich in SiO₂ and Al₂O₃, that, when activated by alkaline solutions, form an amorphous aluminosilicate material, responsible for the high mechanical resistance, while system b) (Me₂O-MO-Al₂O₃-SiO₂-H₂O) produces a C-S-H gel forming calcium-rich compounds (Glukhovsky, 1994; Alonso and Palomo, 2001). In recent years, several authors have reported research related to a large number of aspects on alkaline activation-based binders (Pacheco-Torgal et al., 2010), such as, among others: dependence on the nature of the origin of the materials, since binders activated by alkalis synthesized from calcined sources have a higher compressive strength than common raw materials (Xu and Van Deventer, 2000; Barbosa et al., 2000), immobilization of toxic metals (Vance and Perera 2009; Vinsova et al. 2007; Provis, 2009a), reaction mechanisms and hydration products (Bakharev, 2005; Mackenzie et al. 2005; Weng et al. 2005), the role of calcium in alkaline activation (Alonso and Palomo, 2001; Yip et Van Deventer, 2003; Yip et al. 2005; Buchwald et al. 2005), manufacturing operations (Pinto, 2004; Pinto et al. 2002), and also, the development of lightweight materials in construction (Wu and Sun, 2007; Pacheco-Torgal et al. 2010).

3.1-COMPOSITION

In general, Davidovits expanded the concept of alkaline activated materials by formulating a specific composition of silica (SiO₂) and alumina (Al₂O₃) reactive constituents of aluminosilicates that, by reacting among themselves in a strong alkaline
environment, generates three types of bonds: Si-O-Al-O; Si-O-Al-O-Si-O and Si-O-Al-
O-Si-O (Pinto, 2006; Davidovits, 1991). In (Figure 3), alkali-activated slag exemplifies alkali-activated cements with high calcium content, with SiO₂ + CaO representing more than 70% of the total weight of the ligand constituents and Al₂O₃ with less than 20%. The main reaction product is formed in the earlier states of hydration and is called C-S-H (hydrated calcium silicate). Alkaline products N-A-S-H (hydrated sodium alumino silicate) and C-(N)-A-S-H (resulting from the replacement of Ca²⁺ by Na⁺) are formed more slowly due to the fact that the crystallization process is more time-consuming (Krivenko, 2017).

![Figure 3 - Alkali activation mechanism (Garcia-Lodeiro, 2015 apud Keane, 2021)](image)

Alkaline activation involves a chemical reaction between various aluminosilicate oxides with silicates under various highly alkaline conditions, producing Si-O-Al-O bonds of polymer matrix, thus indicating that any Si-Al materials can be activated by álcali (Pacheco-Torgal; Castro-Gomes and Jalali, 2010).

### 3.2- PERFORMANCE

Regarding durability, alkaline-activated materials show an improvement in the reduction of both permeability and porosity, because an accessible porosity allows the entry of liquid and gaseous which can trigger chemical changes inside the concrete (Pinto, 2006). Alkaline cements and alkaline hybrid cements, in terms of durability, (Adam, 2009a; Bacuvčík, 2017; Wang et al., 2020) show, in most cases, pc-like behavior, although it is true that they stand out for their excellent behavior against acid attack and their extraordinary fire resistance (Donatello, 2014; Palomo, 2021).

These indicators contribute, to a large extent, to the performance of this type of material. Associated with the results of a number, albeit limited, of life cycle analysis of alkaline activation technology, they lead to the conclusion regarding the potential of this material as a partial or total substitute for Portland cement (van Deventer et al., 2010). A reasonably extensive research program carried out in Germany (Buchwald et al. 2005a; Weil et al., 2007; 2009) provided much information on the selection of precursors and mixing designs for a variety of materials generally based on geopolymers. However, geographical specificity plays a significant role in a thorough life cycle analysis and
therefore indicates a need for further studies in different locations, and a wide range of mixing projects covering the broader spectrum of (Alkaline Activated Materials) AAMs (van Deventer, et al., 2010)

In the mid-1950s, and in the context of a demand for Portland cement alternatives in the former Soviet Union, Glukhovsky began investigating ligands used in ancient Roman and Egyptian structures (1994). Based on these observations, he developed binders called "soil-cement", combining aluminosilicate residues, such as various types of slag, with alkaline solutions of industrial waste to form an alternative binder to cement. From the 1960s on, Glukhovsky Institute in Kiev, Ukraine, became involved in the construction of apartment buildings, railway dormants, stretches of roads, pipes, drainage and irrigation channels, floors for dairy farms, slabs and precast blocks, using alkali activated blast-oven slag (Rostovskaya et al., 2007; Shi et al., 2006). Further studies of sections taken from these original structures showed that these materials have high durability and a compact microstructure (Xu et al., 2008). A large number of patents and standards have been produced for previous slag mixtures, but this documentation has been largely inaccessible in the West. The Kiev team continued under the supervision of Professor Pavlo Kryvenko to develop mixing projects for different raw materials and applications (Krivenko and Talling 1996).

In the late 1970s, Davidovits coined the term "geopolymer" for a variety of alkali-activated metakaolin binders that did not envolve (Ordinaire Portland Cement) OPC-type phases in their chemistry [16]. That soon gained interest from governmental and industrial organizations in the U.S. (Malone et al., 1985). During the 1980s and 1990s, an OPC/AAM hybrid concrete called Pyrament was developed and commercialized. This concrete reached a resistance of 20 MPa in four hours and was used in the 1991 Gulf War for rapid placement of runways. In 1993, Pyrament was applied to 50 industrial facilities in the U.S., 57 military installations, and in seven other countries (Davidovits, 2008; Wheat 1992). In 1994, the U.S. Army Corps of Engineers published a study showing that the Pyrament performed better than expected for other high-quality concrete (Husbands, 1994).

However, in 1996, the commercialization of Pyrament was terminated, not for technical reasons, but because of restructuring and corporate issues related to its manufacturer's parent company. Unfortunately, this event tarnished the image of AAMs concrete and much of the operational experience gained with Pyrament was lost. Pyrament was about twice as expensive as OPC concrete (Magrath, 1991) and still had a high OPC content, since its goal was technical performance rather than lower CO₂ emissions or cost reduction. Thus, it is clear that geopolymer and alkaline activation technology have been known in the cement and concrete industry for approximately 50 years, but commercial acceptance of the technology so far has been limited until very recently. These obstacles, which have hindered the growth of the AAMs industry, are quickly being eliminated due to global concerns about CO₂ emissions and climate change, so the growing geopolymer industry in some parts of the world is unable to cope with market demand due to complications in developing a high-volume supply chain in parallel, or possibly in competition with, the Portland cement concrete industry, which is highly vertically integrated (van Deventer et al., 2010).

A commercial life cycle analysis was carried out in Australia and was coordinated by commercial producers of inorganic polymeric concrete. This analysis compared AAMs
concrete with a standard Portland cement product available in Australia in 2007, and it was based on the comparison of binder to binder and of concrete to concrete (van Deventer et al., 2010). The linkage comparison showed an 80% reduction in CO$_2$ emissions, while the concrete comparison showed a slightly higher savings of 60%, as the energy cost of producing and transporting aggregates was identical for both materials. However, this study was again specific to a single site and product, and it will certainly be necessary to conduct further analysis of new products as they reach the stages of international development and commercialization (van Deventer et al., 2010).

4-LIFE CYCLE OF MATERIALS

Life cycle assessment methodology (LCA) analyzes the potential impact of materials, products and technology. Its procedure is normalized to the 2006 14040 series international standards. The life cycle is defined as the consecutive and interconnected stages of a product system, from the acquisition of raw material or generation of natural resources to the final disposal (ISO 14040, 2006). Life cycle assessment is the compilation and evaluation of inputs, outputs and potential environmental impacts of a product system throughout its life, structured in four main steps: Definition of objectives and scope, Inventory analysis, Impact Assessment and Interpretation (Ouellet-Plamondon and Habert, 2015; Deutsches Institute fur Normung, 2006). The environmental impact of geopolymers remains a recent open debate, especially as they are presented as an alternative to conventional concrete. Initially, (Duxson et al., 2007; Ouellet-Plamondon and Habert, 2015) stated that CO$_2$ emissions in the production of geopolymers were much lower than in OPC production. These statements were based on two indicators, which are the reduction of water use and the non-need for superplasticizer additives. This first assessment did not take into account the impact of industrial waste production, such as ash and blast furnace slag, which are not accessible to all countries, e.g. Europe (Habert, 2013). The first ACL of geopolymers was published by Weil (et al., 2009) who compared 1m$^3$ of ice-defrost resistant concrete of class XF2 and XF4 according to DIN EN 206-1 (Deutsches Institut fur Normung, 2005; German Institute for Standardisation, 2012; Portuguese Quality Institute, 2005) and 1m$^3$ of geopolymer with a slag/fly ash with ash ratio of approximately 80/20 cured at room temperature. The LCA considered three impact categories: Abiotic Depletion Potential (ADP), Global Warming Potential (GWP) and Cumulative Energy Demand (CED). The geopolymer surpassed CEM I concrete in global warming potential (GWP) by a factor of 3, and with a similar impact, in abiotic depletion potential (ADP) and also in cumulative energy demand (CED). Habert et al. (2011) show, however, that the production of geopolymer concrete has a greater environmental impact in other categories than global warming due to the production of sodium silicate. There are environmental indicators to consider: Abiotic depletion; Global warming; Destruction of the ozone layer; Ecotoxicity of marine water; Terrestrial ecotoxicity; Human toxicity; Eutrophication; Acidification and Photochemical Oxidation (Ferreira, 2004). Life cycle assessment is the compilation and evaluation of inputs, outputs, and potential environmental impacts of a product system throughout its life. It has four main stages; 1-Definition of objective and scope, 2-Inventory analysis, 3-Evaluation, and 4-Impact interpretation, as shown in (Figure 4) (Deutsche Institut für Normung, 2006)
The relationships between the parts of ISO 15686 and life cycle planning of buildings can be seen in (Figure 5), which specifies their general principles for planning lifespan of a building or other built asset, and presents an indicative structure for the execution of such planning. These general principles can also be used for decision-making on maintenance and replacement requirements, also serving as a guide for other parties, including requirements and guidance on estimating the life cycle of a building's components, which contribute to that of buildings.

**Figure 4** - Key steps on life cycle assessment, adapted from International Standard ISO 14040 (2006)

**Figure 5** - Relations between the parts of ISO 15686 and the planning of the useful life of buildings, adapted (Lair et al., 2001).
4.1-PROJECTIONS

The projections or estimation of lifespan according to ISO 15686 can be addressed by reading three north-south vertical axes, according to Figure-6. The first axis originates from test data and degradation model (part-2), the second axis from reference lifespan under certain conditions (part-8), combined with the indications on data and production documentation (part-9) and finally the third axis originates from the documentation detailing information on lifespan (part-7).

These three vertical axes finally converge, directly predicting lifespan, when under the same conditions of use and or for the same performance of the components, or, in the absence of these latter obligations, the Factor method for the proper projection of lifespan may be used.

Figure 6 - Methods and tools for defining the prediction of life, adapted (Lair et al., 2001).

4.2-METHODOLOGIES AND PLANNING

In the field of methodology and planning, complex problems are common and can range from data collection to - decision making. Some examples include meteorology, toxicology, traffic management and others, to which experts take different approaches, starting in most cases, with product data collection, its definition, its environment and others, so that they can understand and model all the phenomena involved (Talon et al., 2006). Finally, from this modeling, decision elements are taken from the recommendations, alternative comparison elements, evaluation parameters to be used and others. In this approach, and especially with life cycle assessment, one of the biggest obstacles to decision making is the ability to deal with both uncertain and heterogeneous information, often with management of uncertainty and ignorance, for which the solution is in the co-exploration of data, i.e. "Simultaneous exploration of multiple points of view in a data or in a method to process it" (Talon et al., 2006). This approach enriches the analysis (complementary information, analysis and conflict exploration) and conducts summarized and consensual information. Managing uncertainty and ignorance also
increases the reliability of the results. In order to bring these procedures together, as suggested in Figure 7, the following four main steps apply: (1) - Data collection (2) - Data organization and modeling (3) - Fusion procedure and (4) - Reportage (Talon et al., 2006).

![Figure 7 - Proposed approach to methodology and planning. Adapted (Talon, et al., 2006).](image)

In steps 1 and 2 several models with different points of view are analyzed, including the evaluation of construction products; in step 3 the data are linked by extracting the consensual information in the viable format for the stage 4 (Talon et al., 2006). Currently, there are

Several tools and methods for durability assessment (field tracking studies, expert opinion, accelerated tests, natural weathering, modeling (reliability models...), materials science... But its use implies some problems: non-reproducibility and traceability of field tracking studies, subjectivity of expert opinion, duration of accelerated tests and natural weathering, relevance of the torture test, quality and amount of knowledge required for modeling (these studies are available only for simple and known materials or products, for one or two degradation phenomena). Data collection consists of collecting all available durability data from the product or one of its components, in its intended environment or in one of its parts. Indeed, two types of lifetime data can be collected: - Data that fully represents the system in your predicted environment. - Data representing only a part of the system (component), and/or a part of the predicted environment (a degradation phenomenon). All this information is dispersed (variety of sources and studies), in a dissimilar way (scale and formalism of uncertainty) and with different quality (force of hypothesis...) (Talon, et. al. 2006, p. 187-8).

5-THE DURABILITY AND PROPERTIES OF ENGINEERING

The durability of these AAM materials is precisely the determining factor that differentiates them from Portland cement (Duxson et al., 2007). To these advantages should be added the fact that these binders allow the reuse of some materials such as waste from mines and quarries, and still have a high capacity for the immobilization of toxic and radioactive waste, which gives them an indisputable environmental value (van Deventer et al., 2010). There is a direct relationship between durability and different comprehensive engineering properties, including geopolymeric structure, surfaces and interfaces, chemistry, physics, aquatic environment, additives, binders, alkaline metals, the electric charge balance of cations, the electrical load of the surface, composition, execution, synergy and competition, the role of the ligating phase, diffusion transport, nucleation and crystallization, precipitation of impurities, alkaline-ground metals, particles that do not react, the encapsulated cations and others, all shown in figure 8, a broad relationship between durability and engineering properties.
Figure 8: Schematic diagram showing some of the relationships between the various areas that constitute technology of geopolymeric ligands. Adapted (Duxson et al., 2007).

6-CHEMICAL MATRIX DEGRADATION PROCESSES

Alkaline cements and alkaline hybrid cements, in terms of durability, show, in most cases, pc-like behavior, although it is true that they stand out for their excellent behavior against acid attack and their extraordinary fire resistance (Adam, 2009a; Law et al., 2015; Bačuvčík, et al., 2017; Wang et al., 2017; Wang et al., 2020; Donatello et al., 2014). Even though most concrete structures are not subjected to highly acidic conditions, there are some situations where this becomes a problem and, in these circumstances, the lifespan of concrete structures can be severely reduced. Acid rain (Xie et al., 2004), acid sulfate soils (Soroka, 1979; Floyd et al., 2003), animal use (de Belie et al., 2000; Bertron et al., 2007) and industrial processes (Chaudhary and Liu, 2009) can produce acids that could potentially degrade concrete. However, the most economically important industrial cause of acid-induced damage in infrastructure elements is corrosion by biogenic sulfuric acid, which usually occurs in sewage pipes (Davis et al., 1998; Monteny et al., 2000; Parker 1947), and is an important focus of research in several long-standing studies around the world with various technical solutions (whether related to the manipulation of concrete by the pipe itself or by the use of coatings) developed and implemented (Fourie et al., 2009; Saricimen et al., 2003; Scrivener et al., 1999). Many of the procedures used
in acid attack testing of concrete are similar, in a general sense, to leaching tests, several of which specifically involve exposure to acidic conditions.

The most important mode of acid attack on a binder, whether based on OPC or AAM, takes place via degradation of concrete by ion exchange reactions. This leads to a breakdown of the matrix nano- and microstructure, and weakening of the material. In some cases this can be extremely rapid and serious, and the acidic conditions may be induced by either industrial or biogenic processes. In a laboratory test, different parameters are adjusted in order to mimic the real-life situation as closely as possible, or to accelerate the degradation and thus obtain results more rapidly, and the extent and manner to which this acceleration is applied will influence the test results. These parameters include the pH and concentration of the acidic solution, the physical state of the sample (monolith or powder; paste mortar or concrete), temperature, rate of acid replenishment, presence or absence of mechanical action/flow, alternate wetting and drying, alternate heating and cooling, and pressure. These parameters should be carefully selected, and should always be reported together with test results (Abora et al., 2014, p. 208-9).

In addition, the choice of the selected degradation measure (loss of strength, loss of mass, depth of penetration) can lead to different conclusions about the relative performance of concrete types, in particular when the binder chemistry is quite different between samples (Lloyd et al., 2012). A combination of several relevant indicators will often be required. The preparation and conditioning procedures of the sample and maturity at the time of the test are also extremely important.

AAMs have often been advertised as being highly acid resistant; this has proven to be, in fact, an important driver for academic and commercial developments in this area for many years (Wastiels et al., 1993; Buchwald et al., 2005b). However, many of the claims submitted have not been sufficiently tested to allow the use of AAMs in acid exposure applications where long-term performance is critical. Furthermore, the applied tests were generally designed for Portland cement classifiers, have not yet been validated for AAMs and can therefore provide the expected information on "real world" performance (van Deventer et al., 2010; Provis et al., 2009b). Due to the use of different raw materials, curing durations, mixing designs, sample formats, acid exposure conditions and performance parameters in each published study on acid resistance of AAMs, it is very difficult to make an immediate meaningful comparison between the results obtained. Many of the test methods used vary drastically from the conditions foreseen in service; for example, 70% nitric acid (Rostami et al., 2003) at room temperature, or 70% H₂SO₄ at 100 °C (Buchwald et al., 2005b). Tests in conditions close to those foreseen in service are expected to provide more representative results, but with potentially longer test durations. This is more or less universal in the development of accelerated test methods.

7-DEGRADATION PROCESSES BY MASS TRANSPORT

Currently, the chemistry understanding of steel corrosion within AAMs binders is still probably insufficient to allow the development of specific testing methods for the chemistry of these materials (Bernal et al., 2014). This is especially the case for AAMs materials based on GBFS (Granulated Blast Furnace Slag) or other metallurgical slag containing sulfates, which generates a reducing environment within the linker and causes complexities in electrochemistry that are not yet well understood (Bernal et al., 2014). It
will certainly be necessary to further analyze and understand the mixtures in large-volume GBFS with OPC (which have reached a more advanced stage in the analysis of AAMs, due to the greater maturity of this research topic), in order to obtain a deeper understanding of the influence of sulfate chemistry in the corrosion rates of steel as to its complexity (Bernal et al., 2014).

The effects of the presence of high concentrations of alkalis and, in particular, the interaction between carbonation, chlorides and alkalis, as well as the relationship between the transport properties and the chemistry of steel corrosion at the rebar-paste interface, provide a fruitful ground for researchers in the coming decades, and much remains to be understood in this area (Bernal et al., 2014, p. 249).

Thus, it seems important to recommend that whatever the test methods selected for the analysis of AAMs, a complete report of the conditions and experimental details in each published study is essential to provide the reader with the ability to understand and use the results of the work (Bernal et al., 2014). This is universally important in implementing durability testing, but it is particularly critical in areas such as corrosion testing, where there are many misunderstood parameters that can potentially influence the results obtained in all tests performed (Bernal et al., 2014). In most reinforced concrete applications, the predominant modes of structural material failure are more related to the degradation of the built-in steel reinforcement than to the alloyer itself (Bernal et al., 2014). Thus, a key role played by any structural concrete is the supply of cover depth and sufficient alkalinity to keep steel in a passive state for a long period of time (Bernal et al., 2014). Loss of passivation usually occurs due to the entry of aggressive species such as chlorides, and or loss of alkalinity by processes such as carbonation (Bernal et al., 2014). This means that the mass transport properties of the hardened ligand are essential to determine the durability of concrete, and therefore the analysis and testing of the properties related to the transport of alkali-activated materials are fundamental (Bernal et al., 2014). Sections dedicated to the chemistry of steel corrosion in alkali-activated binders and efflorescence (which is a phenomenon observed in the case of excessive alkaline mobility) are also incorporated into the study and discussion due to their close connections with transport properties due to their close connections with the transport properties (Bernal et al., 2014).

7.1-PERMEABILITY AND POROSITY

There are numerous studies on the relationship between microstructures and permeability of Portland cement-based concrete, including some presented and revised in detail in (Powers and Brown yard, 1947; Garboczi 1990; Lu et al., 2006; Bernal et al., 2014). Many different porosimetric techniques are available, some of which have been formally standardized in different jurisdictions, but most of which rely on commercially available or institutionally built laboratory equipment for sample analysis (Bernal et al., 2014). Also, in order to obtain results and information in standardized and non-standardized analytical protocols, there are original publications with complete experimental details in each instance, namely the reports presented in RILEM TCs 116-PCD (Kropp et al., 1995) and 189-NEC (Torrent et al., 2007), which contain descriptions and analysis of many of the available techniques on the permeability of concrete (Bernal et al., 2014).

Gas sorption analysis (usually using nitrogen, argon, or helium) can also be used to calculate pore size distributions and surface areas through various algorithms such as the
popular Brunauer-Emmett-Teller (BET) (1938) and Barrett-Joyner-Halenda (BJH) (1951). Mercury intrusion porosimetry (MIP) is also widely used in the study of hardened phases of the ligand. Some controversy involves the applicability of MIP to complex pore geometries, such as those observed in building materials (Diamond 2000), but these complications may also provide opportunities for more advanced analytical procedures such as multicycle MIP and Wood metal intrusion for a better understanding of the pore geometries in the material (Kaufmann 2009; 2009B; Lloyd et al., 2009).

Water permeability analysis also provides useful information when applied to hardened concrete – either where the water is forced into the sample under pressure or where capillary suction is used to draw water to the sample. Each of these classes of test is able to provide information which is essential in understanding the structure and durability of AAM concretes, and in predicting their in-service performance (Bernal et al., 2014, p. 225).

There is no universally applicable technique that can provide a complete multiscale characterization of a complex material, such as an AAMs or concrete linker; a more complete toolkit of techniques is required to get details on the length scales of interest. The BJH method for pore size distribution calculations has been standardized in several jurisdictions (Barrett et al., 1951; Deutsches Institut für Normung, 1997; International Organization for Standardization, 2006) for porous materials in general but not with specific application for cements or building materials. Although this method has been compared unfavorably, in recent years, to more advanced methods of converting gas sorption data into pore size distribution information (Neimark and Ravikovitch, 2001; Metroke et al., 2012), it remains the method that has been more widely applied for the extraction of gas pore size distribution information and sorption data for alkali-activated binders. Lloyd (et al., 2009) e Zheng (et al., 2010) used the BJH technique to observe the refinement of pores in AAMs derived from fly ash with increasing activator concentration, which is consistent with the conceptual understanding of the formation of these materials.

7.2-CAPILLARITY

Capillarity tests have shown that the BFS (Blast Furnace Slag) concrete pore networks activated with alkali are sufficiently refined and tortuous to lead to a fairly low extent of capillary sorptivity in these materials (Adam 2009a; 2009b; Hákkinen, 1993), although porosity was, in most cases, similar or higher to that of comparable Portland cements. The use of a higher module activator (Bernal et al., 2010), or a lower water content (Collins and Sanjayan, 2008) in alkali-activated BFS systems, reduces water absorption rate and sorption decreases with increased curing time in humid conditions (Collins and Sanjayan, 2008). Attempts were also made to model the flow rate through BFS concrete pore networks activated with alkali, describing capillary pores as an elliptical model shape pore (Collins and Sanjayan, 2010a). This was successful to some extent, although it is known that the actual geometry of the alkali-activated agglutinating pore network involves significant "cartridge" effects, where larger radius pore volumes are accessible only through narrow necks (Lloyd et al., 2009; Provis et al., 2012). Very high capillary suction of highly porous alkali-activated metakaolin or natural pozzolan-based binders is potentially problematic in many applications and can lead to efflorescence if alkali movement is not properly controlled (Kani et al., 2012). However, it also specifies
possible applications in thermal control, providing a water source for evaporative cooling (Okada et al., 2009). Another standardized test method is the Initial Surface Absorption Test (ISAT), as described in BS 1881-208 (British Standards Institution, 1996), which uses a narrow capillary placed in contact with the surface of a sample of dry concrete (or in service) and calculates concrete sorptivity through the rate of movement of the water from the capillary to the material. This test has the advantage of being relatively fast (approximately 1 hour per sample), but it does not seem to have been applied to alkali-activated concrete in the currently available literature. Similar methods include the EN 772-11 test (European Committee for Standardization, 2001), which is specified for mortars and also measures the water flow of an external pipe in the pore structure of the material.

7.3-CARBONATION

There is limited knowledge about carbonation in AAMs (Bernal et al., 2014). Byfors et al. (Byfors et a., 1989) identified higher carbonation rates in F-concretes (GBFS activated by sodium silicate), when compared, in accelerated tests, with common concretes (Bernal et al., 2014). These results are in accordance with the observations of Bakharev (et al., 2001), who also reported greater susceptibility to carbonation in AAMs concrete prepared with sodium silicates and BFS than in reference concrete with an ordinary Portland cement base, when evaluated under accelerated carbonation conditions (Bernal et al., 2014). On the other hand, Deja (2002) identified that GBFS mortars and alkali-activated concrete showed carbonation depths comparable to those obtained for Portland cement reference samples, along with increased compression strengths and longer CO$_2$ exposure time (Bernal et al., 2014). This was associated with a refinement of the pore structure, as carbonates precipitated during carbonation reaction. This was more noticeable in silicate-based activated samples than in sodium carbonate-activated samples (Bernal et al., 2014).

It is important to note that accelerated carbonation of the specimens in this study was induced using a carbonation chamber at a relative humidity of 90% and fully saturated with CO$_2$ (Bernal et al., 2014). These results should be interpreted very carefully because, in such high relative humidity, pore saturation in these samples is such that even when exposing AAMs to extremely severe CO$_2$ concentrations, the carbonation reaction does not develop in the same way as it would at lower relative humidity values (Bernal et al., 2014). This is consistent with the patterns identified by Byfors et al. (Byfors 1989), which established that the carbonation of AAMs is faster when materials are exposed to lower relative humidity (Bernal et al., 2014).

The relative humidity conditions in which the carbonation of AAMs is evaluated are critical, as the shrinkage by drying and subsequent carbonation can be favored in low humidity conditions and can induce microcracks in the material, increasing the progress of carbonation (Bernal et al., 2014). Studies conducted by Bernal (2009) in GBFS/concretes with metakaolin mixture showed that the progress of carbonation and the consequent increase in total porosity are legitimately higher when the samples are carbonated at 65% relative humidity, compared to carbonated samples at values of 50 or 80% relative humidity (Bernal et al., 2014). However, after longer periods of carbonation exposure, the effect of relative humidity becomes less relevant, and slightly increased carbonate depths are identified with increased relative humidity (Bernal et al., 2014). For carbonation tests of GBFS and GBFS/metakaolin activated by calcium silicate, where the
samples were not submitted to the drying process before the test, a separate measurement of the water absorption of non-carbonated samples provided a good indication of how the drying effects during the test period would probably slow the early stages of carbonation (Bernal et al., 2012). Testing samples with low water absorption (i.e. when the pore network is initially saturated and refined) at high relative humidity provides a very low carbonation rate in the early stages of the test, as the carbonation rate of the saturated binder is relatively slow, and subsequently there is an acceleration of the carbonation process as the drying front enters the sample and allows the continuation of carbonation (Bernal et al., 2014). Very little attention has been paid to the evaluation of carbonation retraction in construction materials in general, a fact that is associated with the stresses induced in cement pastes as a consequence of the formation of carbonation products, initially in the pore network and then in the advanced carbonation conditions in the binder gel (Alexander and Wardlaw, 1959).

There is no specific standard method to measure carbonation retraction, but this behavior was analyzed (Houst, 1997) only in a few studies, and procedures similar to those described in ASTM C596-09 (2009) or ASTM C1090-10 (2010) are adopted (Bernal et al., 2014). In this case, shrinkage is measured at different times of CO₂ exposure to correlate the carbonation depth with any dimensional changes presented by the samples. The extension of carbonation shrinkage in AAMs is, in terms of the available literature, completely unknown. However, Shi identified that during 75 days of exposure of a GBFS paste activated by alkali at 15% CO₂ and 53% relative humidity, cracks were observed a few days after the start of the carbonation test, as a combined effect of shrinkage by drying and shrinkage by carbonation (Shi 2003) (Bernal et al., 2014).

8-FULL-SCALE APPLICATIONS

While recent and growing demand for greener alternatives to traditional concrete has led to more research on AAMs, this technology and its application in construction projects are not new. The development of AAMs was evident post-World War II, with first applications in the 1950s (CEN, 2011); Aydin and Baradan, 2014) when concrete, based on explosion slag, activated only with calcium hydroxide (Ca(OH)₂) or in combination with sodium sulfate (Na₂SO₄), called "Purdocement", was first used in Belgium for the construction of several buildings (Aydin Baradan, 2014). Since then, numerous structures have been built, including hydraulic works, pavements, roads, conventional precast products, and more recently, large-scale projects molded in-situ, as follows (Table-1).

<table>
<thead>
<tr>
<th>Year</th>
<th>Location</th>
<th>Construction work</th>
<th>Material</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1952-1959</td>
<td>Brussels, Belgium</td>
<td>Parking 58</td>
<td>Purdocement (GBFS + PC activated by Ca(OH)₂ or Na₂SO₄)</td>
<td>(Aydin, 2014)</td>
</tr>
<tr>
<td>1966</td>
<td>Odessa, Ukraine</td>
<td>Drainage collector No. 5</td>
<td>Alkali-carbonate activated GGBFS concrete</td>
<td>(CEN, 2011)</td>
</tr>
</tbody>
</table>
Table 1: Examples of full-scale applications, adapted from (Rossi et al., 2023)

<table>
<thead>
<tr>
<th>Year</th>
<th>Location</th>
<th>Project Description</th>
<th>Concrete Type</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1988</td>
<td>Yinshan County, Hubei</td>
<td>6-storey office and retail building</td>
<td>Sodium sulfate-activated Portland-slag cement concrete</td>
<td>(CEN, 2011)</td>
</tr>
<tr>
<td>2009</td>
<td>Melbourne, Australia</td>
<td>Salmon St Bridge</td>
<td>E-Crete precast footpath panel segments (180 precast footway units)</td>
<td>(van Deventer and Provis, 2014)</td>
</tr>
<tr>
<td>2009</td>
<td>Brisbane, Australia</td>
<td>Musgrave Plant site bridge</td>
<td>EFC precast bridge decks</td>
<td>(Buchwald et al., 2015)</td>
</tr>
<tr>
<td>2010</td>
<td>Melbourne, Australia</td>
<td>Thomastown Recreation and Aquatic Center</td>
<td>E-Crete footpaths and driveways</td>
<td>(van Deventer and Provis, 2014)</td>
</tr>
<tr>
<td>2012</td>
<td>Melbourne, Australia</td>
<td>Melton Library</td>
<td>E-Crete precast panels and in-situ works</td>
<td>(van Deventer and Provis, 2014)</td>
</tr>
<tr>
<td>2013</td>
<td>Queensland, Australia</td>
<td>Global Change Institute (GCI) Building, University of Queensland</td>
<td>EFC – 33 precast floor beam-slab elements</td>
<td>(Buchwald et al., 2015)</td>
</tr>
<tr>
<td>2013</td>
<td>Irvine, California, USA</td>
<td>Sustainable concrete solar-powered house</td>
<td>Precast alkali-activated fly ash concrete members</td>
<td>(Rossi et al., 2023)</td>
</tr>
<tr>
<td>2013</td>
<td>Yuzhong District,</td>
<td>Chongqing Research Institute of Construction</td>
<td>Cast in-situ alkali-activated GGBFS concrete</td>
<td>(Rossi et al., 2023)</td>
</tr>
<tr>
<td></td>
<td>Chongqing, P.R China</td>
<td>Science office building</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>Toowoomba,</td>
<td>Toowoomba</td>
<td>EFC-cast in-situ heavy-duty pavements</td>
<td>(Buchwald et al., 2015)</td>
</tr>
<tr>
<td>2020</td>
<td>Wageningen, Netherlands</td>
<td>Cycle bridge</td>
<td>RAMAC (prefab)</td>
<td>(Yang, 2022)</td>
</tr>
<tr>
<td>2021</td>
<td>Chatham, UK</td>
<td>Chatham railway station (step-free access foundation)</td>
<td>Cemfree-300 m3 cash in-situ</td>
<td>(Tempest, 2015)</td>
</tr>
<tr>
<td>2021</td>
<td>Le Havre, FRA</td>
<td>Grand Port Maritime du Havre</td>
<td>Exegy-concrete barrette (17 m depth)</td>
<td>(Rossi et al., 2023)</td>
</tr>
</tbody>
</table>

9-CONCLUSIONS

Recent studies of climate change show that new cementitious materials are known to be responsible for a lower CO \(_2\) emission level than Portland cement; The question of whether geopolymer concrete or AAMs are durable remains unanswered, and constitutes an obstacle to wider commercial adoption; Regarding durability, alkaline materials stand out for their reduction of both permeability and porosity and their excellent behavior against acid attack and extraordinary fire resistance. Currently, the understanding of the chemistry of steel corrosion within the AAMs binders is still likely insufficient to allow the development of specific test methods for the chemistry of these materials, since the effects of the presence of high concentrations of alkali and, in particular, the interaction between carbonation, chlorides and alkalis, as well as the relationship between the transport properties and the chemistry of steel corrosion at the regal-paste interface, provide a fruitful ground for researchers in the coming decades, and there is still much to be understood in this field of research.

ACKNOWLEDGMENTS

The authors thank all persons and entities who directly or indirectly contributed to the purpose of publishing this work.
REFERENCES


Pozzolans in Concrete, ACI SP114, Pp. 1429-1444. Trondheim, Norway. American Concrete Institute, 1989.


Parker, C. Species of Sulphur Bacteria Associated with the Corrosion of Concrete. Nature 159, 439–440 (1947). https://doi.org/10.1038/159439b0


