

Durability of concrete with alkali-activated materials, a short literature review

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Abstract

The alkali-activated materials are being understood as the best chance to replace the Portland cement to become the concrete industry greener in terms of CO₂ emissions. However, these alternatives binders face challenges, among others related to durability. The present work regards to a short literature review about the durability in concrete produced with binders that are alkali-activated materials. The mechanisms of degradation are discussed, namely due to acid attack, capillarity, carbonation, permeability, porosity and steel corrosion. Comparison to the concrete permeability, porosity and steel corrosion. Comparison to the concrete that used Portland cement as binder is frequently used.

Author Keywords. Slag, Alkaline Activation, Corrosion, Durability.

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1. Introduction

The production and consumption of ordinary Portland cement is responsible for 5 to 8% of total anthropogenic CO₂ emissions of which 95% of CO₂ is developed during cement production (C. Ouellet-Plamondon 2014), (Huntzinger DN and Eatmon TD. 2009), (Worrell E 2009). Moreover, this production has been contributing for decades to the degradation of the terrestrial platform through the exploitation of calcareous and clayey materials. To face the environmental problem, new alternative materials have been considered to replace the Portland cement – the supplementary cementitious materials. However, to achieve carbon neutrality by 2050, the binders obtained from alkaline activation (also known as alkali-activated materials or as alkaline cement) seem to be the most reliable alternative as it is expected to reduce CO₂ emissions (Habert G 2010). However, the concrete made of alkali-activated materials lack of standards. Subsequently, concerns regarding durability, knowledge of useful life-cycle planning methodologies, analysis of applicable standardization, approach and determination of estimated lifetime as well as the implementation of measures to promote durability, and also the studies of technical, environmental, socio-economic and financial impact are frequently questioned. This review is a contribution on the road of the alkali-activated materials to replace the Portland cement in concrete. Here, a review of the literature focused on the durability of products produced with alkali-activated materials is done. The present work is part of a large project where the main objective is the development of concrete elements using activated alkaline materials, namely the

Municipal Solid Waste Incineration Slag being used as a precursor of the alkaline reactions.

2. Durability of alkali-activated materia materials

According to Van Deventer et al. (2011) , the question of whether geopolymer concrete or alkali-activated materials are durable remains another important obstacle to broader commercial adoption. That means, it is the question, not the answer, that remains 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 (C. Shi 2006)-(J. Deja 2002) . As for the results, in addition to the existing structures and in service, it is appropriate to ask what elements and time periods will be needed as proof of their 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 (R. Taylor 2010). Also according to Van Deventer et al. (2011), in this context, alkali-activated systems have the unenviable task of showing themselves to be durable when the final measure, the presence of decades-old structures, is in the end 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 work under normal environmental conditions for a period of decades or more (Jannie S.J. VAN DEVENTER 2011). Predictive models depend on concepts that include mass transport through porous means, reaction kinetics, and particle packaging. A deficiency of this approach to try to "prove" durability is that 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 what is considered a "long-term" test is at least a smaller order of magnitude than the expected service life of most concrete structures. 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 (Jannie S.J. Van Deventer 2011).

Regarding durability, materials with alkaline activation are highlighted in the reduction of both permeability and porosity, because an accessible porosity allows the entry of liquid and gaseous agents capable of promoting chemical changes inside the concrete (Amândio Teixeira Pinto 2006) . Alkaline cements and alkaline hybrid cements in terms of durability (Law 2015) ,(Wang 2020) show, in most cases, Portland Cement -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 A 2021).

These indicators contribute to a large extent to the performance of this type of materials associated with the results, although a limited number of life cycle analyses of alkaline activation technology (Van Deventer JSJ 2010). A reasonably extensive research program carried out in Germany (Buchwald 2005)(Weil 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 there is a need for further studies in

different locations, in addition to a wide range of mixing projects covering the broader spectrum of alkali-activated materials (Van Deventer JSJ 2010).

In the mid-1950s, and in the context of a demand for Portland cement alternatives in the former Soviet Union, Glukhovskiy began investigating ligands used in ancient Roman and Egyptian structures (Glukhovskiy 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, the Glukhovskiy 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 2007) ,(Shi 2006). Further studies of sections taken from these original structures showed that these materials have high durability and compact microstructure (H. Xu 2008).

For Duxson et al.(2007) , the durability of these alkali-activated materials is precisely the determining factor that differentiates them from Portland cement (Duxson 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 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 incapsulates and others, in a broad relationship between durability and engineering properties.

3. Degradation Processes

3.1. Degradation due to steel corrosion

Currently, the chemistry understanding of steel corrosion within alkali-activated binders is still probably insufficient to allow the development of specific testing methods for the chemistry of these materials (Susan A.Bernal 2014) .This is particularly the case for alkali-activated 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 (Susan A.Bernal 2014).

It will certainly be necessary to analyze and understand the mixtures in large-volume granulated blast furnace slag with Portland cement (which have reached a more advanced stage in the analysis of alkali-activated materials, 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 (Susan A.Bernal 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 of research (Susan A.Bernal 2014).

Thus, it seems important to recommend that whatever the test methods selected for the analysis of alkali-activated materials, 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 (Susan A.Bernal 2014).

This is universally important in implementing durability testing, but is particularly critical in areas such as corrosion testing, where there are so many misunderstood parameters that can potentially influence the results obtained in all tests performed (Susan A.Bernal 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 the concrete itself (Susan A.Bernal 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 (Susan A.Bernal 2014).

3.2 Carbonation

There is limited knowledge about carbonation in alkali-activated materials (Susan A. Bernal 2014). Byfors et al. identified higher carbonation rates in concretes with granulated blast furnace slag activated by sodium silicate when compared, in accelerated tests, with common concretes (Susan A. Bernal 2014).

These results are in accordance with the observations of Bakharev et al. , who also reported greater susceptibility to carbonation in concrete prepared alkali-activated materials with sodium silicates and granulated blast furnace slag than in reference concretes to the common Portland cement base, when evaluated under accelerated carbonation conditions (Susan A. Bernal 2014).

On the other hand, Deja identified that granulated blast furnace slag mortars and concretes activated with alkali showed carbonation depths comparable to those obtained for Portland cement reference samples, along with increased compression strengths and longer CO₂ exposure time (Susan A. Bernal 2014). This was associated with a refinement of the pore structure, as carbonates precipitated during the carbonation reaction. That effect was more noticeable in silicate-based activated samples than in sodium carbonate-activated samples (Susan A. Bernal 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 temperature of 90% and fully saturated with CO₂ (Susan A. Bernal 2014). These results should be interpreted very carefully because, in such high relative humidity, pore saturation in these specimens is such that even when exposing alkali-activated materials to extremely severe CO₂ concentrations, the carbonation reaction does not develop in the same way as it would be at lower relative humidity values (Susan A. Bernal 2014), Byfors et al.

3.3 Acid attack

Alkali-activated materials and alkaline hybrid cements in terms of durability (Adam 2009), (Law 2015), (Bacuvčík 2017), (Aiguo Wang 2017) , 2020 (Wang 2020) show, in most cases, Portland Cement -like behavior, although it is true that they stand out for their excellent behavior against acid attack and their extraordinary fire resistance (Donatello 2014).

Although most concrete structures are not subjected to highly acidic conditions, there are some situations where this becomes a problem and, in these circumstances, the life of concrete structures can be severely reduced. Acid rain (Xie 2004), acid sulfate soils (Soroka 1979), (Floyd 2003), animal use (de Belie 2000), (Bertron 2007) and industrial processes (Chaudhary 2009) can produce acids that can 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 1998),(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 2009) ,(Saricimen 2003),(Scrivener 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 linker, whether based on Portland cement concrete or alkali-activated materials, occurs through the degradation of concrete by ion exchange reactions. This leads to a breakdown of the nano and microstructure of the matrix and the weakening of the material.

3.4 Permeability, porosity and capillarity

There is no universally applicable technique that can provide a complete multiscale characterization of a complex material, such as an alkali-activated materials or concrete; a more complete toolkit of techniques is required to get details on the length scales of interest.

The BJH (Barrett-Joyner-Halenda) method for pore size distribution calculations has been standardized in several countries (Barrett 1951) (International Organization for Standardization 2006), but for porous materials in general and 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 2001) (Metroke 2012) ,this remains the method that has been applied more widely for the extraction of gas pore size distribution information sorption data for alkali-activated binders. Lloyd et al. (Lloyd 2009) and Zheng et al. (Zheng 2010) used the BJH technique to observe the refinement of pores in alkali-activated materials derived from fly ash with increasing activator concentration, which is consistent with the conceptual understanding of the formation of these materials.

Capillarity tests have shown that the granulated blast furnace slag concrete pore networks activated with alkali are sufficiently refined and tortuous to lead to a fairly low extent of capillary sorvability in these materials (A. A. Adam 2009),(Häkkinen 1993), (Rodríguez 2008) (S. A. , M. de G. R. , P. A. L. , P. J. L. , R. E. D. , D. S. Bernal 2011), (Häkkinen 1992), (S. , de G. R. , D. S. , R. E. Bernal 2010),(A. A. , M. T. C. K. , P. I. , L. D. W. Adam 2009) , although porosity was, in most cases, similar or higher to that of comparable Portland cements.

The use of a higher module activator (S. A. , M. de G. R. , R. V. , P. J. L. Bernal 2010) or a lower water contente (Collins 2008) in alkali-activated granulated blast furnace slag elements, reduces water absorption rate and sorption decreases with increased curing time in humid conditions (Collins 2008) . 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 (Najafi Kani 2012) but also provides possible applications in thermal control, providing a water source for evaporative cooling (Okada 2009).

4. Discussion

As results and discussion, we highlight the problems about the emissions of Carbon Dioxide (CO₂) and about the Durability of the materials obtained with alkaline activation. As for CO₂ emissions, they show a growth trend, due to the expected increase in the production and consumption of Portland cement by China, India, Middle Eastern Countries and Developing Countries in the order of approximately 4.3000 million tons in the year 2030 and approximately 5.2000 in 2050.

Regarding durability, activated alkaline materials stand out in reducing permeability and porosity. In addition, they exhibit excellent behavior against acid attack and have an extraordinary resistance to fire.

Still in durability, the problem of degradation mechanisms is a permanent concern, despite the variety of techniques available for pore analysis at microscales within materials and classified into the categories of one-dimensional, two-dimensional and three-dimensional analysis.

Among these categories, there is no universally applicable technique that can present a complete multiscale, since a more complex set of techniques is required to obtain details on all the width scales of interest.

One-dimensional analysis of porosity in the nanometer to micron range is usually conducted by gas sorption (most commonly the Barrett-Joyner-Halenda technique, BJH), direct penetration measurements (air, water, and chloride penetration being the most commonly applied), and another using Mercury Intrusion Porosimetry (MIP).

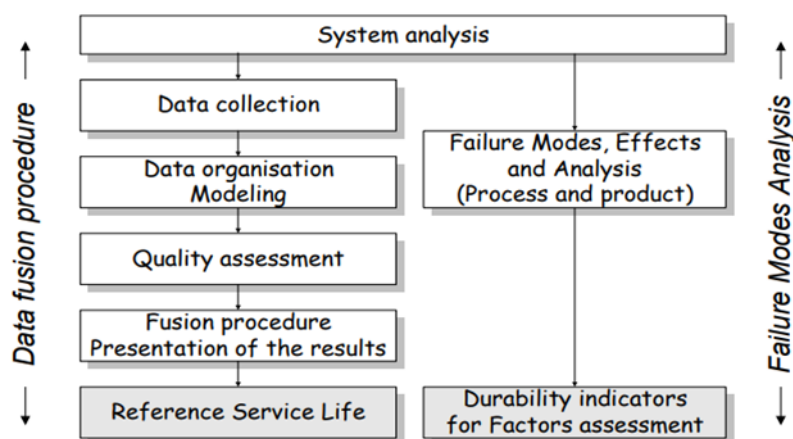


Figure 1: Durability evaluation methods and tools (J. LAIR, 2001)

4.1 Figures

Today society is thinking about "Sustainable Development", in order to avoid quality problems in civil construction, to take into account social, environmental and economic aspects, encouraging the development of methods and tools to assess the durability of construction materials, both traditional and innovative products (Jernberg 1997). In this context, two complementary tools were developed by (Lair 2000), being 1-Data fusion procedure (left part of Figure 1) and 2-Analysis of Failure Modes and Effects (right part of Figure 1) (J. LAIR 2001).

5. Conclusions

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