Korozija čelika u alkalno-aktiviranim materijalima uzrokovana kloridima: pregled stanja područja

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Chloride-induced corrosion of steel embedded in alkali-activated materials: state of the art

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Abstract

Alkali-activated materials are a group of alternative binders based on aluminosilicate precursor and an alkali activator. Since precursors are mostly waste materials and by-products, AAMs are consideredto be a valid and more environmental-friendly alternative to Portland cement. Although the AAMs show good performance, there are not enough studies in the literature about their long-term durability performance related to chloride ingress and embedded steel corrosion. The issue of this paper is to highlight the main difference between OPC and the different types of AAMs, and to give a short introduction about the state of art of this embedded steel corrosion.

Key words: alkali-activated material, review, durability, steel corrosion, chloride ingress, chloride binding capacity

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Sažetak

Materijali aktivirani alkalijama su skupina alternativnih veziva na bazi aluminosilikatnog prekursora i alkalnog aktivatora. Oni bi u budućnosti mogli biti zastupljeni kao valjana i ekološki prihvatljiva alternativa portland cementu. Osim što su AAM pokazali dobre rezultate, u literaturi nema dovoljno studija o dugotrajnoj izvedbi klorida i ugrađene korozije čelika. Problem ovog rada je osvijetliti glavnu razliku između OPC-a i različitih tipova AAM-ova i dati kratak uvod o stanju ove ugrađene korozije čelika.

Ključne riječi: alkalijski aktivirani materijal, pregled, trajnost, korozija čelika, prodor klorida, sposobnost vezanja klorida

1   Introduction

Alkali-Activated Material (AAM) is a general name used to indicate a group of alternative binders, obtained by the reaction between an aluminosilicate source, usually an industrial by-product such as slag from iron and steel production, coal fly ash from thermoelectric plants, among others, and an alkali activator which is usually a concentrated aqueous solution of alkali hydroxide, silicate, carbonate or sulfate [1-3]. Since AAMs are based on industrial byproducts and waste materials, they are considered to reduce the CO_2 emission coming from the cement clinkerisation process, and also divert industrial byproducts from landfilling. Another important advantage to use byproducts is the preservation of natural materials which are normally used in production of Portland cement clinker. It is for these reasons that AAM have received a lot of interest from the scientific community as one of the options when considering more sustainable alternatives to ordinary Portland Cement (OPC).

The AAMs can be distinguished into two different categories based on the final phase assemblage [1-5]:

- Low Ca systems – based on the activation of a precursor with low Ca content, such as fly ash or metakaolin, where the main reaction product is a three-dimensional alkali-aluminosilicate hydrate (N-A-S-H) type gel;
- High Ca systems – based on the activation of a precursor with high Ca content, such as slag, where the main reaction product is calcium-aluminosilicate hydrate (C-A-S-H) type gel.

The AAMs show many engineering characteristics comparable to OPC, and published studies report higher stability when exposed to elevated temperature [6], higher resistance against chemical attack [7-9] and potentially better resistance to freeze-thaw cycles [10, 11], all compared to OPC. However, being a comparatively young engineering material, the quantity of available durability data is limited, and the long-term performance of structures made with AAMs is yet to be determined. Available knowledge on degradation mechanisms from OPC cannot be directly transferred to alkali-activated systems, due to the difference in reaction products, pore solution chemistry, and microstructure of the matrix. Additionally, what makes it more challenging is that any generalization in the case of AAMs is practically impossible since all the parameters of the system differ for each AAM, depending on the type and chemistry of precursor material and the type and amounts of activators used [1,4,5,11]. Among the degradation mechanisms that seek attention is the de-passivation of steel reinforcement embedded in alkali-activated concrete.

The most common causes of reinforcement corrosion are localized de-passivation of the steel surface due to chloride ingress, and/or more general de-passivation due

to acidification of the pore solution as a result of carbonation of the cement paste [13]. In either of the two cases, behaviour of steel when embedded in concrete can be divided into three phases:

- passivation phase – during which passive film is formed on the surface of the steel,
- activation phase or corrosion initiation - during which passive film losses the stability and finally breaks down, and
- degradation phase or corrosion propagation - during which corrosion products start to precipitate on the surface of the steel, leading to concrete cracking.

In all of these three phases chemical and physical properties of concrete surrounding the steel play a crucial role. It can therefore be expected that once steel is embedded in AAM, all three phases will occur with some particularities as compared to OPC.

2 Passivation phase – Formation of passive film

The passive film is the external layer formed on the surface of reinforcing steel after contact with an alkaline environment, like cement. It is a protective film formed at the beginning of the embedding of steel, but the quality and the stability of that film depend on the exposure duration and the chemical composition of the passivating solution. In a classical OPC system in which black steel reinforcement is embedded, the passive film has a bi-layer structure:

- inner layer Fe^{2+}rich layer oxy-hydroxide (1-3 nm)
- outer layer Fe^{3+}rich hydroxide film (5-10 nm) [17].

The behaviour of steel in AAMs is more complex because the passivation process is regulated by the redox potential of the steel and oxygen availability, pH and chemistry of the surrounding environment: the different precursor material and activator of AAM change this equilibrium. The most important factor that affects the stability of passive film is the pH and, consequently, the chemical composition of pore solution. The pore solution of a system is a function of the composition of the blend; for that reason, the chemical characteristics of SCMs (Supplementary Cement Material) (i.e. chloride binding capacity, alkalinity) significantly affect the corrosion rates of steel in concrete.

2.1 pH value

The pH is the main factor influencing the stability of the passive film on the steel. Gouda et al. [22] found that using different NaOH and $Ca(OH)_2$ in solutions with different pH the passive film is stable until pH 12.1-11.75. The leaching of OH^- from

AAS and, probably, also the accelerated carbonation could reduce the pH of AAS faster than OPC [24]. Shi et al. [25] showed that AAS has a higher pH at early ages, but after one year of exposure to chloride environment pH value decreases faster than in the case of OPC. Similar was observed in the study by Ma et al. [27]. The pH value decreased sharply near the surface zone of AAS due to the outward diffusion from AAS into the chloride solution. In OPC, $Ca(OH)_2$ would dissolve in the pore solution to buffer its alkalinity; this explains the reason for a constant pH value in the OPC concrete at different depths. However, $Ca(OH)_2$ is not one of the reaction products of AAS, and for that reason the loss of alkalinity is more severe in the case of the AAS concretes, particularly in the near surface zone, as can be seen in Figure 1.
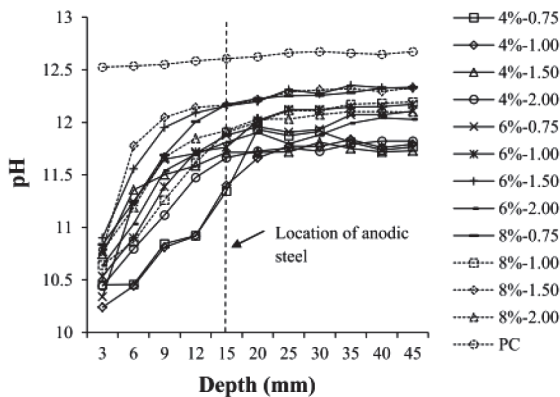

Figure 1. pH profiles determined at the end of the chloride ponding exposure regime [27]

The hydroxyl ion concentration of OPC is typically in the range of 0.53 M to 0.71 M. Scott and Alexander [20] showed the changing concentration of OH^- for AAMs blends and OPC after 90 days of maturation; in the system based on OPC it increases by 2.5-2.8 times, the blends contained fly ash, silica fume or slag show a more constant value or a decrease that is approximately 5 times lower than OPC. This reduction in OH^- concentration inhibits the capacity of the systems to preserve the stability of the passive film on the steel surface. Babaee and Castel [28] displayed that pH of AAM is lower than OPC; pH value of AAM was around 11.5 at the level of the reinforcing bar compared to the widely accepted pH of about 12.5 for uncarbonated OPC.

2.2 Sulfide content

It is not only the pH value of the solution that has the paramount influence on the stability of the passive film, it is also the chemical composition of pore solution [23].

In the case of low-Ca systems, Mundra et al. [14] showed that despite the different chemical composition of precursor materials, this system has a broadly similar passivation process to that of OPC systems. However, the high-Ca systems based on blast furnace slag, or the high-volume blends of slag with Portland cement, can still have a conventional passivation preocess or show a different behavior mostly due to the sulfide content in the slag. The general range of sulfide concentrations in pore solutions for slag replacement levels up to 90 % in PC blends appear to be in the range of 110 to 300 mg/l in addition to thiosulfate ($S_2O_3^{2-}$), found by Glasser et al. [21], and these concentrations are similar in AAS cements [12]. At the beginning the sulfides are oxidised to sulfate by the oxygen available in the system, thus depleting the oxygen concentration at the steel, creating a reducing environment and leading to a more negative value of corrosion potential [18, 35], as seen in Figure 2 a). The reducing environment would favor the formation of Fe(II) rather than Fe(III), which forms the α-Fe_2O_3 responsible for passivation [20]. Instead of an iron oxide passive film, the precipitation of mackinawite ($Fe_{1+x}S$) on the steel surface occurs [19, 24]. According to this the passivation process would be inhibited. Still some studies have shown that corrosion rate generally decreased with the increase of the concentration of sulfide due to the reducing environment provided by sulfide, Figure 2 b) [27]. Since the steel is embedded in an alkaline solution devoid of oxygen, this absence at the steel surface inhibits the cathodic reaction and the corrosion is controlled [26].
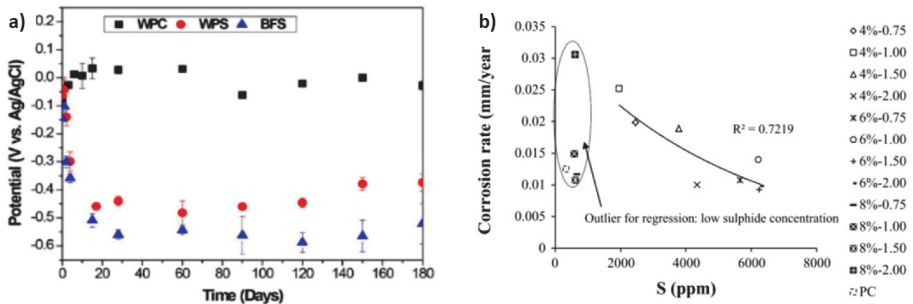

Figure 2. a) Evolution of the potential values as a function of time, for steel embedded in AAS (BFS), OPC + slag (WPS) and Portland cement (WPC) mortars immersed in water [35], and b) Relationship between the corrosion rate and the sulphide concentration [27]

3   Activation phase – Corrosion initiation

The steel surface works as a mixed electrode composed of anodes and cathodes electrically connected through the body of the steel itself, upon which coupled anodic and cathodic reactions take place. Concrete pore water functions as an aqueous medium, i.e. a complex electrolyte [13, 29]. The anodic reaction is an oxidation process that depends on the pH and the presence of aggressive anions, such as Cl^-. The cathodic reaction is a reduction process that depends on the O^{2-} availability and the pH [13]. There are numerous parameters affecting time of corrosion initiation and hereafter only two main influences (critical chloride content and chloride binding) will be considered in detail.

3.1   Critical chloride content

The presence of chloride ions will contribute to the breakdown of the passive layer, while other anions such as OH^- are responsible for its stability and have inhibiting properties. There is believed to be a point at which the concentration of aggressive ions overcomes the inhibiting ions and 'corrosion' can initiate, and this is called the critical chloride content (C_{crit}) [15].
Babaee and Castel [31] analysed in depth the Cl^- threshold value for different AAM. According to the authors the C_{crit} of AAM based on fly ash is 0.19-0.69 (% by binder mass), compared to the 0.2-0.4 % by mass of binder for OPC reinforced concrete [16]. For slag-dominated samples, when increasing slag content the C_{crit} decreases independently of the alkali content or the sodium silicate activator modulus, which is indicating a less-developed passive film in these binders that can be broken down comparatively easily. The lower stability of the passive layer can be attributed to the oxidation of sulfide anions, which was explained in previous chapter. The AAMs with higher alkaline activator have higher chloride thresholds due to a better dissolution of the precursors that generated a more homogeneous binder. As a result, a less permeable passive layer formed around the bars which took longer to break down. Another influential factor could be the presence of more OH^- ions that reacted with the iron cations to form the iron hydroxide layer around the bars [31].

3.2   Chloride binding capacity

The value of total chlorides does not always coincide with the free chloride (Cl^- in pore solution) because during the corrosion process the chloride can move through the pore solution or/and bind with the hydration products of the system; it is simultaneously present in the pore solution and in the cement matrix. The amount of bound chloride depends on the percentage chloride binding capacity (P_{cb}) of the system.

In OPC, the Cl may be bounded through physical bonds or chemical bonds. The first bond depends on the amount C-S-H, amount of activator, w/b ratio and amount of aggregates and can be released into the pore solution on diluted conditions. The second one depends on the amount of C_3A and C_4AF from which are formed the Friedel's salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$) and other AFm phases. The AAMs show different behavior due the chemical and mineralogical compositions. The absences of C_3A and C_4AF hinder generally the precipitation of Friedel's salt [31, 26], but chloride could bind in the AFms and other layered phases that do form [32]. According to Ke et al. [32] hydrotalcite-like (Mg-Al) phases and strätlingite (AFm structure) can take up chloride from highly alkaline solutions with different initial [Cl$^-$]/[OH$^-$] ratios. In hydrotalcite-like phases the Cl$^-$ is mainly adsorbed (~90 %) and the amount ion-exchanged is just 10 %, while the strätlingite has less dominant surface adsorption, and lattice substitution of chloride also takes place [31, 32]. Khan and Kayali [33] demonstrated that the blast furnace slag influences more than OPC the binding capacity: increasing the amount of slag the free chloride content is reduced and P_{cb} increased, this suggests that the Cl$^-$ bound in AFm or hydrotalcite is higher than absorbed in C-S-H. Maes et al. [30] explained that increasing the amount of slag in an OPC blend the Friedel's salt formation increases because it is linked to the Al_2O_3 content. The chloride binding ability gradually decreases with increasing the quantity of sulfate in blended systems because SO_4^{2-} has high affinity for the interlayer of hydrotalcite, more than Cl$^-$.

In low-Ca AAM systems, the N-A-S-H favors more the adsorption of Cl$^-$ than C-(A)-S-H. Alkali binding increases as calcium content decreases with fly ash addition, hence reducing the alkalinity in the pore solution. High alkali binding capacity is also attributed to the surface charge of the N-A-S-H, which attracts more ions from the surrounding pore solution [29, 27]. Lee and Lee [34] found a correlation between the aluminosilicate gel and the chloride-binding capacity in AAMs; increasing the aluminosilicate gel with the depth, the P_{cb} increases; therefore, the increase of bounded Cl with the depth is linked with the aluminosilicate gel content in AAMs; the chloride-binding capacity increases with an increase in the fly ash content and with a decrease in the slag content because the addition of fly ash results in greater physical absorption of chloride compared to the C-(A)-S-H gel due to the higher surface area of the aluminosilicate gel in the alkali-activated fly ash, Figure 3.a) The NaOH concentration has an important role during the chloride binding because more chloride ions were bound in geopolymer with higher NaOH concentration than with lower NaOH concentration because the physical binding of chloride ions increases due the greater geo-polymerisation, Figure 3 b) [29].
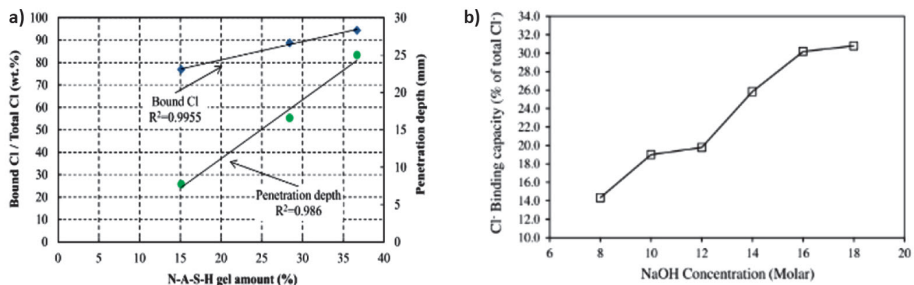
Figure 3. a) Bound chloride-to-total chloride ratio (%) and penetration depth (mm) over the N-A-S-H gel amount (%) in alkali-activated fly ash-slag samples [34]; and b) The effect of sodium hydroxide (NaOH) concentration on chloride binding capacity of fly ash-based AAM concrete [29]

4 Conclusion

The alkali-activated material systems have different chemical and mineralogical composition compared to OPC, which strongly influences all phases of corrosion process. In the case of low-Ca AAM, the higher amount of N-A-S-H gel rather than C-S-H favors chloride adsorption, but the absence of C_3A and C_4AF hinder the formation of AFm phases that can give chemical binding. In the case of high-Ca AAM, such as AAS systems, a high content of sulfide generates reductive environment in which thinner and potentially less durable passive film is preferentially formed. In such systems, the main reaction product is C-A-S-H, and the high Ca and Al contents favor the AFm precipitation and the chemical chloride binding. Although both types of AAMs showed binding of chlorides, the main difference is in the gel phases. The finer structure of C-A-S-H reduces the chloride penetration but also the physical binding, while the porous structure of N-A-S-H increases the penetration and the adsorption of chlorides.

The different chemical composition of AAMs makes it difficult to use the OPC standards as a reference. The variability is high for each type of system and depends on the type of precursor and the specific blends made. Establishing and validating durability and corrosion testing methods for alkali-activated concretes remains the major obstacle to their commercial adoption in demanding structural applications, and ultimately their acceptance in national and international regulatory standards for structural concrete. Finally, even though AAM attract a lot of attention due to the potential CO_2 saving, calculations on CO_2 emissions are more complex than merely considering the volume of byproducts substituting cement. Some of the materials used as precursors must be milled which also consumes a lot of energy and emits some CO_2. Additional challenge lays in the fact that most of these materials are cur-

rently considered as waste, which makes their transport and industrial application difficult. The properties and use of these materials in the future must be regulated by international standard, such as EN 450 for fly ash.

Acknowledgment

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