

BINDERS ALTERNATIVE TO PORTLAND CEMENT AND WASTE MANAGEMENT FOR SUSTAINABLE CONSTRUCTION – Part 1

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ABSTRACT

The paper represents "a state of the art" on sustainability in construction materials. The authors propose different solutions to make the concrete industry environmentally friendly in order to reduce greenhouse gases emissions and consumption of non-renewable resources. The part 1 of present paper focuses on the use of binders alternative to Portland cement, including sulfoaluminate cements, alkali-activated materials and geopolymers. Part 2 will be dedicated to traditional Portland-free binders and waste management and recycling in mortar and concrete production.

Introduction

With the dawn of twenty-first century, the world has entered into an era of sustainable development. As a consequence of this, concrete industry has to face two antithetically needs: how it can feed the growing population needs being – at the same time - sustainable? Sustainability in construction industry can be achieved through three different routes (Fig.1): reduction in consumption of gross energy, in polluting emissions and in not renewable natural resources. Different strategies can be identified along these three routes to make concrete sector more environmentally friendly (Fig.2): a) using alternative fuels and raw materials to reduce CO₂ emissions to produce Portland cement; b) replacing Portland cement with low-carbon supplementary cementitious materials (SCMs); developing alternative low-carbon binders (alkali-activated materials, geopolymers and calcium sulphoaluminate cements); c) reducing natural resource consumption through to waste management and recycling (1–3).

The part 1 of present paper deals with use of binders alternative to Portland cement. Part 2 will be dedicated to waste management and recycling in mortar and concrete production.

1. Alternative binders to Portland cement

Different alternative binders to traditional Portland cement have been proposed: sulfoaluminate cements, activated alkaline binders and geopolymers.

1.1. Sulphoaluminate cements

Calcium SulphoAluminate cements (CSA) were applied since the end of the 1950's (4). Then in the mid-1970s, CSA cement was produced in an industrial scale in China by burning limestone, bauxite and gypsum at 1300 ~ 1350°C (5). In China, CSA cements are treated as a special binder with rapid setting, shrinkage compensation and high early-age strength. The main phase of CSA is tetracalcium trialuminate sulphate or ye'elimite (C₄A₃S̄). The amount of ye'elimite in CSA cement usually varies from 20% to 70%. Apart

from ye'elimite, belite (C_2S) is another main phase in CSA cement; while secondary phases may include C_4AF , C_3A , $C_{12}A_7$ and C_6AF_2 (6). CSA cement is a sustainable cement when compared with OPC (7,8), since less limestone is required due to the low CaO content in ye'elimite phase (7,9,10). Moreover, more gypsum or anhydrite ($CaSO_4$) is needed to prepare CSA cement; therefore, the CO_2 released in CSA cement production process is much less than that for OPC production (11). Secondly, its calcination temperature is 100 ~ 150°C lower than that of OPC, which helps reduce 15% coal consumption with respect to OPC (12). Thirdly, CSA clinker is porous, which makes it easier to be ground (13) and this further reduces energy consumption. However, the use of CSA cement to replace OPC 100% might encounter some adversities such as over-short setting time (12), low pH (14), high price (15) and expansion risk (7). Thereby, blending CSA with OPC might combine their advantages and improve properties such as expansion and setting time (16), passivation ability of steel and porosity (14).

The hydration process of CSA cement has been studied (17–21). The first hydration reaction in the presence of gypsum ($C\bar{S}H_2$) is:



The formation of ettringite ($C_6A\bar{S}_3H_{32}$), Aft, mainly takes place in the first hours (22). When gypsum is depleted, ye'elimite forms monosulphate ($C_6A\bar{S}_3H_{12}$): AFm. Hydration of belite occurs at later age due to its low reactivity. Because the hydration products of ye'elimite contain amorphous AH_3 , reaction of belite in the presence of AH_3 will form stratlingite (C_2ASH_8) rather than C-S-H (23). Most of the ye'elimite and gypsum react in first 7 days; while most of belite could be unhydrated even at 90 days (7). In case of blended CSA/OPC cement, their hydration products highly depend on the ratio of OPC/CSA. For low OPC/CSA ratio, the hydration of OPC takes place in several days later after casting (24). Alite (C_3S) in OPC cement can react with AH_3 , that is the hydration product of ye'elimite at early stage, to form stratlingite (C_2ASH_8) and portlandite (CH) at early stage (16). For high OPC/CSA ratio,

alite can bring about C-S-H and portlandite; then the portlandite together with gypsum may change the hydration reaction of ye'elimite to form $3C_6A\bar{S}_3H_{32}$. The short setting time of CSA concrete is due to the quick and large formation of ettringite in the first hours (25). Content of anhydrite in CSA concrete can influence early-age compressive strength as well; increasing anhydrite content means more ye'elimite phase which reacts at early age and therefore forms more hydration products (26).

Study performed on CSA cement paste revealed that a bimodal pore distribution was developed since the very early age; lower porosity is dominant, but not connected with higher porosity (27). Moreover, the average pore size of CSA concrete is smaller than that of OPC. The porosity of CSA mortar decreased with the increase of anhydrite content and the decrease of w/c ratio (26). A series of factor can influence the expansion of CSA concrete (7,28), but ye'elimite content plays an important role. When the portion of ye'elimite is more than 50% in CSA cement, expansion, cracking and loss of strength appear at later age; the proper content of ye'elimite seems to range from 30% to 40% (29).

2.2 Alkali activated materials

Alkali-Activated Materials (AAMs) were developed starting from the 1940's (30). They are obtained by reaction of an alkali metal source with amorphous or vitreous calcium-aluminosilicate precursors. The former is used to increase the pH of the reaction mixture thus accelerating the dissolution of the powders, while the composition of the latter determines the physical-chemical processes that produce hardening (31,32). Microstructures, workability, strength and durability of AAMs can be tuned by a proper combination of activators and precursors. Mix Design of AAMs includes materials from both natural sources (metakaolin: MK, pozzolans: P) and by-products (slag: GGBS, fly ash: FA and paper sludge: PS). AAMs can be classified on the nature of precursor (CaO-SiO₂-Al₂O₃ system) into two main categories: (a) high calcium and (b) low calcium. When aluminosilicate sources (MK, FA) are used, a (Na,K)₂O-Al₂O₃-SiO₂-H₂O system is generated. It can

be considered a subset of AAMs that is usually referred as geopolymers, characterized by a peculiar pseudo-zeolitic network structure (33–35). When slag is used as precursor, a $(\text{Na,K})_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system is produced. It is activated under moderate alkaline conditions (36,37) and hardening is produced by the formation of a C-A-S-H gel. A combination of the preceding two systems is also possible (38,39) where hardening is due to the formation of C-A-S-H and (N,C)-A-S-H gels network (40).

The reactive powder used to produce the calcium-rich binder is blast furnace slag originated from the purification process of iron ore to iron (41). GGBFS is a mixture highly glassy phases with composition close to those of gehlenite and akermanite: (31-38%) SiO_2 , (38-44%) CaO , (9-13%) Al_2O_3 and (7-12%) MgO , and S, Fe_2O_3 , MnO and K_2O with percentages of less than 1%. When it is used to produce AAMs, parameters affecting GGBFS reactivity are the vitreous phase content (85–95%wt), its degree of depolymerization (DP from 1.3 to 1.5) and its specific surface (400–600 m^2/kg) (31).

Slag alkaline activation consists (30–32) in dissolution of the glassy particles, nucleation and growth of the initial solid phases, interactions and mechanical binding at the boundaries of the phases formed, ongoing reaction via dynamic chemical equilibria and diffusion of reactive species through the reaction products formed at advanced times of curing (42,43). At the early ages, alkaline solution reacts with dissolved species generating the outer C-A-S-H. At longer ages, the inner C-A-S-H gel is produced by ongoing reactions of the undissolved portions of the slag particles through a diffusion mechanism (44).

Cations and anions of the activator play a specific role in the activation process. When hydroxides are used the OH^- acts as a catalyst and it is responsible for the pH increase, thus allowing the precursor dissolution and the formation of stable hydrates (45). Slag-based binder can be prepared using 2–4 M solution with Na_2O content less than 5% slag weight to guarantee mechanical properties and reduce efflorescence (46), (47,48)(49). When sodium silicate is used, the gel is characterized by lower Ca/Si and a less ordered structure. In both

the cases gel is composed by coexisting 11 and 14 Å desordered tobermorite-like phases (43), with Ca/Si ratio (0.9–1.2) lower than in hydrated Portland cement system. AFm type phases or strätlingite are formed when NaOH or silicate are respectively used (50,51). If raw materials contain high amount of MgO (52,53), Hydrotalcite ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$) is produced, while in presence of low MgO (<5 %) and high Al_2O_3 contents zeolites are often found in the reaction products (54).

2.3 Metakaolin and fly-ash based geopolymers

As a general statement, metakaolin has been the “model system” for studying the activation process(55–63), of AAMs. MK ($\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) is a natural pozzolanic material obtained by the calcination of kaolin at 500–900 °C (64,65). MK consists of plate-like particles (66) with a specific surface area generally between 9 – 20 m^2/g . MK pastes usually require a liquid/MK > 0.6 by mass (67) and MK mortars need ~1.0 (68,69). In general, MK geopolymers set within 24 h. Conversely, MK geopolymers have a higher reaction rate and a faster strength gain with respect to FA ones (70,71), because of the presence of secondary minerals in the kaolinite clay (72,73), the fineness of particles (74), and the reaction temperature (75,76). The hydrothermal ageing (95°C) because of the major formation of crystalline zeolite, is responsible for the strength loss (71). Moreover, the thermal treatment of MK mixtures at 80 °C accelerates the strength development, but the final strength is lower than that of specimens ambient cured (68). In geopolymers, the $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{H}_2\text{O}$ influence mechanical properties. Compressive strength and Young’s modulus were found to be dependent on alkali type (Na or K) and Si/Al ratio (77), however at the same compressive strength, the authors (70) found that the modulus of elasticity is lower in geopolymers than in OPC mortars. K-based geopolymers produce a higher compressive strength than Na-based ones (78) and the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ increases also the mechanical strength. Davidovits indicated the optimum $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$ are 1 and 4, respectively (79), while most researchers reported an optimum $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 3–3.8

(49,80). The increase of $\text{Si/Al} \geq 3$ leads to chemical instability in air with efflorescence formation on the surface attributed to the high residual free alkali cations (81). Usually, increasing the $\text{Na}_2\text{O}/\text{H}_2\text{O}$ leads to improved dissolution ability and mechanical strength development of clay-based geopolymers (69,78,82,83). Geopolymers prepared only with MK are highly susceptible to shrinkage both at room and elevated temperatures (67,84–88), because of their high water requirement.

Concerning the effect of aggressive/pollutant substances (89–92) on MK concretes durability, Palomo et al. (93) found that MK geopolymers were stable if immersed in seawater, Na_2SO_4 solution (4.4 %), and H_2SO_4 solution (0.001 M) up to 90 days. On the contrary, Mobili et al. (70) noticed cracks formation on MK geopolymers exposed to Na_2SO_4 solution (14 %), not present in FA ones with the same activators. Gao et al. (94–96) found that MK geopolymers remain sound after 28 days in HCl solution (pH 2). The capillary water absorption of MK-based geopolymers is higher than blended blast furnace slag, (97,98) FA or OPC ones (70). Currently, researchers are studying MK-based geopolymers also to produce non-structural plasters with lightweight aggregates for thermal insulation (99–104) and to be used as mortars able to adsorb Volatile Organic Compounds (VOCs) (105–109).

Another trend is to produce geopolymers suitable for refractory applications, adding a foaming agent, H_2O_2 or Al powder (100,110,111). Results show that only Al-geopolymer are successfully converted to crack-free ceramics on heating (110). The partial substitution of MK with FA gives also positive influences both on thermal resistance (112) and compressive strength (100), thanks to the lower water demand and thus the lower free water evaporation. Foams have much lower thermal conductivity (0.15 – 0.4 W/m·K) than the solid geopolymer (0.6 W/m·K) (113). The thermal conductivity increases with the increase Si/Al ratio (114,115), because of the increased connectivity, reduced porosity and finer pore size distribution. Moreover, increasing the K/Al ratio also the foaming efficiency (final

volume/initial volume) increases (116). Geopolymers derived from a K-based activator were more ready to dissolve or degrade compared to an Na-based one both if foamed (117) or not (118–120).

Research field investigated “one-part” MK geopolymers, obtained by adding only water to the dry materials, avoiding the use of caustic solutions, by the calcination of the clay material with a powdered activator, such as NaOH or KOH (121), soluble sodium silicate (122), sodium carbonate (123) or by using an alkali-rich by-product, such as potassium-rich biomass ash (124).

FA is an industrial by-product derived from coal fired power stations with a highly variable composition, dependent on the coal source and burning conditions (125). Particle size distribution, chemical composition and crystalline/glassy phases of the precursor are key factors that need to be understood, since they control the precursor reactivity and solubility in alkaline solutions (126). It was found that the geopolymer microstructure is highly influenced by particle fineness, amorphous phase composition, oxides content (particularly Fe_2O_3 , CaO). The lower $\text{Na}_2\text{O}/\text{SiO}_2$ molar the higher the performances in terms of water absorption, and mechanical properties. Geopolymers showed good thermal stability after firing due to the formation of new crystalline phases. Developing comprehensive knowledge of precursors is a fundamental and critical step in commercializing geopolymer products. For example, a preliminary study showed the use of geopolymer mortars for strengthening of concrete structures (127). As workability is one of the main requirements, the research on superplasticizers suitable for fly ash geopolymers needs be emphasized (128–135).

2.4 Clayey sediments and sludge for geopolymers

Geopolymers are attractive because natural and industrial silico-aluminates wastes may be used as precursors. The exploration for alternative low cost and easily available materials led among others to “normal clays”. Clayey sediments consist of different clay minerals and

they are widely available all over the world, offering a significant reactivity after a thermal activation process (136). Among silico-alumina wastes, reservoir sediments are worthy of consideration. Sediments should be removed periodically to avoid reduction in reservoir capacity. There are more than 7000 large reservoirs in EU, of which 564 are in Italy. These data show that regular dredging operations can produce huge amounts of sediment. In this regard, some possibilities have been explored as raw materials in production of artificial aggregates, bricks and cement (137–142). The extension of these possibilities in the field of geopolymer materials has been studied in several papers (143–145).

SiO_2 and Al_2O_3 are the main components in sediments, while CaO and Fe_2O_3 are present in lower concentrations; K_2O , MgO and Na_2O are present in minimum percentages. The main mineralogical phases detected by XRD analysis are: quartz, calcite, clay phases and feldspars. A pre-treatment of the sediment is always necessary in order to enhance the reactivity in the alkaline environment. The optimal thermal treatment is at $750\text{ }^\circ\text{C}$, in fact the ^{27}Al NMR peak at 0 ppm related to octahedral Al (Figure 3) and absorbance FT-IR peaks at 3697 , 3620 and 3415 cm^{-1} were absent or greatly dampened evidencing the collapse of the ordered clay structure.

Thermally treated sediments were employed to manufacture geopolymer mortars and concrete blocks (146).

The prevailing chemical components of the sediments are silica and alumina, then making sediments good geopolymer precursors. However, within the wide range of natural and artificial silico–aluminates, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ in this case is quite high, such to make the alkali aluminate activation and/or the addition of alumina rich additives an interesting alternative. Aluminate activation was studied (147) with encouraging results to manufacture precast building blocks. As regard alumina-rich additives, water potabilization sludge is another key residue produced by the reservoir management activities. These wastes are based on flocculation-clarification processes using alumina coagulants (148). The amount of sludge

generated and its chemical composition depend mainly on chemical and physical characteristics of the water, the efficiency of the removal process and type and dose of coagulant. The amount of sludge can be roughly estimated in the range of 1-5% of the total amount of untreated water (148). This waste has been studied in literature only in a few studies, mainly with regard to potential reuse in construction industry (146,149–155).

The management of huge amount of sediments coming from dredged activities is an important issue to be solved in many countries worldwide. Clean dredged materials can be used for construction fill, brick or asphalt manufacturing, topsoil and marine projects. Recently, Lirer et al. (156) proposed dredged sediments with fly ashes in the production of geopolymers. Regarding the environmental impact, the values of hazardous elements classify geopolymers as non-dangerous materials. Therefore, these preliminary results suggest that this methodology could represent a starting point for the investigation of possible beneficial uses of polluted sediments in geopolymeric matrices.

2.5 Corrosion behavior in alternative binders-based matrix

Replacement of portland cement with alternative binders, especially CSA cements and AAMs, open the theme of protection of reinforcements in these new concretes (157–159). Data (23) seem to indicate the durability of CSA concretes is at least comparable to that of traditional Portland cement mixtures, but they also evidence the need to perform long-term tests in order to recognize the corrosion protection mechanism. The protective capacity of CSA-matrix (160) is confirmed by the positive experience on structures in China, in which no rebar corrosion occurred after 14 years of exposure. However, few information is given about the actual environmental aggressive conditions. Most of the works available are devoted to the study of hydration products in the very early period but only few papers address the corrosion behaviour of reinforcements by means of electrochemical techniques. Potential measurements performed in a few experimental works evidence difficulties in achieving proper values of passive rebars due to the low alkali content in pore water (161).

The studies on durability of mixtures manufactured with such binders address only few aspects – carbonation and chlorides – neglecting relevant aspects governing the corrosion process (12,27,162,163).

The main hydration product of CSA cement is ettringite that does not provide OH^- . The pH of two pure CSA concretes with 0.5 w/c were respectively 10.23 and 10.53 after 90 days (14). In (161), w/c 0.45 CSA mortar showed low pH around 6. However, a high pH around 13, within first 60 days, has been observed (164) by using a CSA cement paste with w/c 0.8. An exhaustive investigation on two CSA cement pastes with w/c 0.72 and 0.8 revealed that: in the case of w/c 0.72 CSA cement paste, within the first hours, the pH was as low as 10.3 ~ 10.7 due to the fact that the initial saturated pore solution was dominated by aluminate, calcium and sulphate; after 16 hours, calcium and sulphate concentrations decreased noticeably due to the depletion of gypsum, thus pH went around 11.8; after 28 days, the pH value reaches 12.7 due to the ongoing release of alkali ions of CSA clinker and the increase of alkali concentrations caused by the consumption of the pore fluid by the formation of hydrates; while w/c 0.8 CSA cement paste showed a similar trend, but a slight higher pH at each stage (18).

Ettringite is susceptible to carbonation (12,13). It seems that the carbonation resistance of CSA concrete is weaker (Fig. 4) than that of OPC concrete (165). However, the investigation on two CSA concrete samples suggested that the carbonation resistance of CSA concrete is comparable with that of OPC concrete; high-strength CSA concrete has excellent carbonation resistance (166). It was found that the carbonation resistance of CSA mortar increased along with the anhydrite content, as well as the decrease of w/c; meanwhile it was also found that carbonation changed the strength performance of CSA mortar due to the modification of porosity caused by carbonation (26).

The lower chloride penetration resistance of CSA concrete when compared to OPC concrete was observed (12). Conversely, low chloride diffusion coefficients of CSA

concretes with different strengths when compared with their OPC counterparts were obtained (167). To enhance the chloride penetration resistance of CSA concrete, modifying AFm/AFt through varying the gypsum content with the hope to let more AFm bind chlorides, was carried out (168). Besides, the good sulphate resistance of CSA concrete was reported in (12–14). In case of blended CSA cement, it was shown that increasing OPC in blended CSA cement (15%-85%) is possible to improve the pH (169).

Currently, there is very few publications dealing with the passivation of steel embedded in CSA concrete. In reference (161), steel in CSA mortar showed a higher corrosion rate than steel in OPC mortar exposed to 3.5% NaCl solution. Half-cell potential measurement showed that steel embedded in CSA mortar was depassivated, showing high corrosion rate in 3.5% NaCl solution, due to the low pH (around 6) of pore solution of CSA mortar. However, corrosion potential and corrosion rate of steel embedded in w/c ratio 0.55 CSA concrete with a pH value of 11.5 showed the passivation of embedded steel, even in concrete exposed to an environment with 95% R.H. and 40°C or immersed in water (165). In reference (14), it's found that mortar made with 100% CSA cement (pH 11.88) was not capable of passivating steel; however, CSA cement blended with 15% OPC (pH 11.32) was enough to guarantee the passivation of steel.

The pH of alkali activated binders is very high at an initial stage due to the presence of activators, leading to the common conclusion that no corrosion issues can occur. However, the pH tends to decrease under endogenous conditions to values well below the limits for steel passivation in absence of chlorides (170) because such kind of binders consume alkalinity during the hydration process. In addition, very scattered pH values are reported and several doubts have still to be solved in terms of corrosion behaviour of reinforcement (171) due to the very different mineralogical composition of precursors. In addition, the role of alkalinity reservoir should be well taken into account for CSA and AAMs binders which are generally prone to consume calcium hydroxide rather than produce it as Portland cement

do (12). The protectiveness is not only attributable to the pH, but also to own ability of OPC concrete to bind chlorides leading to lower amount of free chlorides. The main factors influence the critical chlorides content for pitting initiation are the alkalinity and the concrete-reinforcement interface characteristics (172–175). The effect of alkalinity on localized corrosion initiation can be described in terms of chlorides-hydroxyl ions critical molar ratio, usually assumed equal to 0.6(157,174–183). The critical chloride threshold in OPC concretes is much higher due to oversaturation of calcium hydroxide (184). This lead to an increase in critical molar ratio at values exceeding 2 (173,185). This difference can be ascribed to the buffer ability by calcium hydroxide. The presence of this phase directly in contact with the carbon steel surface represents a reservoir of alkalinity, which contrasts the pH drop due to localized corrosion initiation.

On the contrary, lot of attention should be paid to innovative binders due to the great compositional variability of the raw materials, usually industrial by-products. Chloride contamination can be not negligible leading to an increased risk of localized corrosion especially in the first period when alkalinity has not yet reached a sufficient level to maintain stable passivity.

Mobili (70) studied also the corrosion behavior of carbon and galvanized bars (186,187) embedded in pure FA and MK geopolymers with the same strength class compared to OPC mortars. During the curing period, geopolymers prolong the active state of rebars, but after 10 days, corrosion rates (v_{corr}) decreased to moderate values (around 10 $\mu\text{m}/\text{year}$) in all mortars (70). During wet/dry (w/d) cycles in 3.5% NaCl solution (188), MK geopolymers showed the greatest corrosion of embedded rebars and the highest consumption of the galvanized coating because of the higher porosity compared to FA and OPC ones (189,190). Aguirre-Guerrero (191) studied the chloride-induced corrosion in OPC concrete coated with an alkali-activated mortar (90% MK (or FA) and 10% OPC); the MK geopolymer coating exhibited the best performances.

Accelerated carbonation ($\text{CO}_2 = 3 \text{ vol.}\%$) on slag/MK geopolymers shows that carbonation occurs faster as MK content increases and leads to a reduction in compressive strength (192). Moreover, accelerated carbonation at 50% CO_2 on MK-based geopolymers forms large amounts of sodium bicarbonate leading to a lower pH of the pore solution; while the formation of sodium carbonate in natural conditions does not lead to a pH below 10.5 after one year (193).

2.5 Reinforcement less sensitive to corrosion

Carbonation or chloride-induced corrosion are the main issues in reinforced concrete structure manufactured with different types of binders. In carbonated concrete without chlorides, stainless steel rebars are passive (194,195). For galvanized steel, the presence of an external layer of pure zinc and its thickness is of primary importance to form a passive film; in contact with alkaline solutions, if the pH does not exceed 13.3, a layer of calcium hydroxyzincate is formed and zinc is passivated (196).

In chloride contaminated concrete, the onset of corrosion occurs if a chloride threshold is exceeded. Even though the measurement of this threshold is not easy, some major factors have been identified: the pH, the potential of the steel and voids at the steel/concrete interface (196). In the case of stainless steels, also chemical composition is important: corrosion resistance is improved by increasing Cr and Mo content, while probably the role of Ni is beneficial in alkaline environments and the Mn appears to have worsening effect (196–201). Galvanized steels has a good resistance to chloride-induced corrosion, even if not comparable to stainless steels: in aerated concrete the critical chloride content is maximum 1-1.5% (196).

Few papers have been published about performances of stainless or galvanized steels in new binders matrix (70,128,189,202,203). Moreover, results are not always consistent. Most of the researchers agree that the chloride concentration in alkali activated slag mortars is

lower than in traditional mortars (128,189). This effect has been attributed to the lower porosity and the different chloride binding capacity: while in Portland cement mortars chlorides form low solubility calcium containing compounds, in geopolymers, since calcium content is very low the chloride binding effect is negligible.

pH of the pore solution is a matter of discussion. Some authors stated, without indicating any practical measurement, that pH is highly alkaline (202) or more alkaline than the traditional mortars (70). On the contrary, other authors reports pH value, measured by leaching method, for alkali activated mortars similar to that of CEM II A-L 42.5 R based mortars (between 12.8 and 13.2), but after exposure to 11 cycles of wetting with chloride solution and drying, the pH of alkali activated mortars was found 10.5-10.7 against 12.2 for cement based mortars, (128).

In (202), corrosion of low nickel (4.3%) manganese (7.2%) austenitic stainless steel with 16.5% Cr is compared with traditional stainless steel AISI 304 (1.4301 according to EN 10088-1) in alkali activated fly ash mortars characterized by high alkalinity (authors reported pH higher than 13, even if few details are provided). Both stainless steels exhibited passive behavior up to 2% of chloride content, while carbon steel suffered corrosion in 0.4% chlorides. In (203), stainless steels (traditional type AISI 304 and low nickel) in carbonated mortars subjected to accelerated chloride exposure suffered localized corrosion. Analysis of rebars after 2 year-exposure showed that in alkali activated slag mortars the behavior was better than in OPC mortars. The authors attributed the improvement to the higher concentration of inhibiting bicarbonate/carbonate ions present in these binders (203). The results are promising but not conclusive: on one hand, chloride content 2% in alkaline mortar (202) is not high enough to evaluate the long-term performance of stainless steel rebars. On the other hand, the results of the paper (203) show a little improvement of corrosion behavior in alkali activated mortars vs traditional ones. Concerning galvanized rebars, it has been

mentioned that geopolymeric mortars can have two opposite effects: a delay in the passivation due to the higher pH (potentially negative) and a reduction of corrosion rate after some cycles of wetting with 3.5% NaCl (70,189). Nevertheless, corrosion rate in alkali activated slag mortars were found to be 50 $\mu\text{m}/\text{year}$. This value would lead to the consumption of the zinc layer (typically 150 μm) in few years, so these results do not guarantee long term performance of the galvanized rebar in geopolymeric mortars.

2.6 Alkali activated materials in repair and conservation

The issue of retrofitting and seismic upgrade of existing masonry buildings and reinforced concrete structures, has become of primary interest, due to the huge architectural heritage all over the world. This topic is extremely complex, especially because of many compatibility issues between existing structures and Portland cement repair mortars (204–207). In fact, use of Portland cement mixtures on masonry structures can cause damages due to the presence of sodium and potassium ions that can promote alkali-aggregate reaction (208) or, in presence of wet environments and sulfur-rich natural stones (209), it could determine development of thaumasite and secondary ettringite, with expansion and cracking phenomena. Another key parameter for repair mortars is the elastic compatibility (210,211): if Young's modulus of repair material is different from substrate, it may create detachments and cracks. Finally, it is not possible to overlook the aesthetic compatibility between the original areas and those involved in maintenance works (212).

Currently, natural hydraulic lime (NHL) represents the only binder that can be used in these contexts due to their high compatibility with the substrates (213–215). However, due to their low mechanical strength, NHL-based mortars often do not meet the elasto-mechanical requirements and, for this reason, are very often mixed with Portland cement.

The use of cement-free alkali-activated materials (AAM), such as ground granulated blast furnace slag (GGBFS), could also be a suitable alternative to Portland cement mixtures (216–219).

The key parameter that regulates most of properties of alkali-activated compounds is the precursor/activator ratio (220–225).

A key aspect for use in maintenance is the possibility to tailor the strength and stiffness with the activator/precursor (226–228); in particular, both the compressive strength and elastic modulus increased due to the high alkali-activator dosage in the mixture. Specifically (Figure 5), weakly alkali-activated GGBFS-based mortars can be used for plasters or masonry mortars while, in presence of high activator/precursor ratios, can be employed for seismic retrofitting or for reinforced concrete structures restoration.

Another key parameter of alkali-activated mortars is elastic modulus (Figure 5); several authors (31,50,229,230) showed less rigidity of GGBFS-based matrix respect to reference mixtures with ordinary Portland cement, at equal strength class. In particular, low activator/precursor determine Young's modulus ranging from 10 and 15 MPa while higher alkaline powders dosages cause an increase in GGBFS-based matrix-stiffness and, consequently, elastic modulus grows up to 20 MPa. This property, in presence of substrates restrain the dimensional contraction of repair mortar, determines the development of low internal tensile stresses and, thus, a lower cracking risk.

In general, alkali-activated mortars and concretes show very high free shrinkage compared to conglomerates manufactured with traditional binders (231). These problems are caused by the large amount of water not involved in the hydration reaction that, by evaporating, creates dimensional contraction and markedly porosity of matrix. Researchers (232) note that by increasing the water/binder, there is a growth in shrinkage due to two factors: the great amount of water able to evaporate and the increase of binder paste/aggregates. In addition, it is possible to note that shrinkage is also influenced by type and contents of

alkaline activators (233). Reduction of shrinkage can be achieved by optimizing the mix with ethylene glycole SRA or calcium oxide expansive agents. In addition, methyl cellulose and starch ether (M.S.) can also be added in order to reduce water evaporation at the fresh state (36,234,235). In particular, the addition of blends based on ethylene glycol and calcium oxide can reduce the free shrinkage about 40% compared to reference GGBFS- mortars without admixtures (Figure 6).

Another issue of alkali-activated materials is the efflorescence caused by excess of sodium oxide remaining unreacted in the material due to a disequilibrium in the mix towards the sodium-based activators. The parameter that influences the quantity of efflorescence is the Na/Al molar ratio; conglomerates with higher Na/Al molar ratios show a higher extent of alkali leaching, indicating a stronger tendency towards efflorescence (236,237).

In conclusion, from the analysis of the strengths and weaknesses of AAMs, it turns out that alkali-activated mortars and concretes can be a reasonable alternative to traditional Portland cement-based mixtures or natural hydraulic lime-based conglomerates for restoration of ancient buildings.

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LIST OF FIGURES

Fig. 1 – Main strategies to make concrete sector more environmentally friendly

Fig. 2 – Reduction of energy and pollutants emission in construction materials production

Fig. 3 – ^{27}Al NMR resonance spectra of Occhito sediment before thermal treatment (a), after thermal treatment at 650°C for 1 h (b), at 650°C for 2h(c), at 750°C for 1 h (d), at 750°C for 2h (e)

Fig. 4 – Time evolution of carbonation depth of CSA and reference OPC concrete under accelerated test (on the left) and indoor exposure (on the right)

Fig. 5 – Compressive strength and Elastic modulus of GGBFS-based mortars manufactured with blend of sodium metasilicate, potassium hydroxide and sodium carbonate (7:3:1) at different activator/precursor ratios

Fig. 6 – Free shrinkage of GGBFS-based mortars manufactured with blend of sodium metasilicate, potassium hydroxide and sodium carbonate (7:3:1) at activator/precursor ratio equal to 0.12 with different type of admixtures (M.S. = methyl cellulose and starch ether; SRA: glycole ethylene-based SRA; CaO: calcium oxide-based expansive agent)