

Review

# Alkali-activated binders: A review

## Part 1. Historical background, terminology, reaction mechanisms and hydration products

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### Abstract

The disintegration of concrete structures made of ordinary Portland cement (OPC) is a worrying topic of increasing significance. The development of new binders with longer durability is therefore needed. Alkali-activated binders have emerged as an alternative to OPC binders, which seems to have superior durability and environmental impact. This paper reviews current knowledge about alkali-activated binders. The subjects of Part 1 in this paper are historical background, terminology and hydration products. The proper terminology to designate these new binders will be discussed. The influence of the prime materials and the type of alkaline activator on the reaction mechanisms and on the nature of the reaction products will be described.

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**Keywords:** Alkali-activated; Binders; Terminology; Reaction mechanisms; Hydration products

### Contents

|                                    |      |
|------------------------------------|------|
| 1. Introduction . . . . .          | 1305 |
| 2. Historical background . . . . . | 1306 |
| 3. Terminology . . . . .           | 1307 |
| 4. Reaction mechanisms . . . . .   | 1308 |
| 5. Hydration products . . . . .    | 1309 |
| 6. Conclusions . . . . .           | 1312 |
| References . . . . .               | 1312 |

### 1. Introduction

It is now accepted that new binders are needed to replace Portland cement (OPC) for enhanced environmental and durability performance. The urge to reduce emissions of carbon dioxide (1 tonne of OPC generates

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almost 1 tonne of CO<sub>2</sub>) and the fact that OPC structures, which have been built a few decades ago, are already facing disintegration problems points out the handicaps of OPC binders. In fact, the number of premature cases of OPC structures disintegration is overwhelming. Mehta [1] mentioned a case of pile foundations disintegrated just after 12 years and also the case of a tunnel in Dubai, which was concluded in 1975 and needed to be completely repaired in 1986. Gjorv [2] mentioned a study about Norway OPC bridges which indicates that 25% of those built after 1970 presented corrosion problems. Another author mentioned that 40% of the 600.000 bridges in the US were affected by corrosion problems, being the cost of the repairing operations estimated in 50 billion dollars [3].

Beyond the durability problems originated by imperfect concrete placement and curing operations, the real issue about OPC durability is related to the intrinsic properties of the material. Presents a higher permeability that allows water and other aggressive elements to enter concrete, leading to carbonation and corrosion problems. It also presents a higher amount of calcium hydroxide, which reacts with acids generating soluble compounds.

So far, research works carried out in developing alkali-activated binders show that this new binder is likely to have enormous potential to become an alternative to Portland cement. These binders are still at the early stage of development and, hence, need further research work in order to become technically and economically viable construction materials.

In this paper the most relevant knowledge about alkali-activated binders will be reviewed. The paper consists of three parts:

- Part 1: Historical background, terminology and hydration products.
- Part 2: About materials and binders manufacture.
- Part 3: Properties and durability.

The subjects of Part 1 are the historical background, the proper terminology to describe this new binder and finally the reaction mechanisms and hydration products of these binders will be characterized.

## 2. Historical background

Table 1 presents a historical background about important events in the field of alkali-activated binders [4]. The development of alkali-activated binders had a major contribution in the 1940s with the work of Purdon [5]. That author used blast furnace slag activated with sodium hydroxide. According to him, the process was developed in two steps. During the first one, liberation of silica aluminium and calcium hydroxide took place. After that, the formation of silica and alumina hydrates would happen as well as the regeneration of the alkali solution.

Table 1

Bibliographic history of some important events about alkali-activated binders [4]

| Author                 | Year | Significance   |
|------------------------|------|--|
| Feret                  | 1939 | Slags used for cement  |
| Purdon                 | 1940 | Alkali-slag combinations   |
| Glukhovskiy            | 1959 | Theoretical basis and development of alkaline cements              |
| Glukhovskiy            | 1965 | First called “alkaline cements”                                    |
| Davidovits             | 1979 | “Geopolymer” term  |
| Malinowski             | 1979 | Ancient aqueducts characterized                                    |
| Forss                  | 1983 | F-cement (slag-alkali-superplasticizer)                            |
| Langton and Roy        | 1984 | Ancient building materials characterized                           |
| Davidovits and Sawyer  | 1985 | Patent of “Pyrament” cement  |
| Krivenko               | 1986 | DSc thesis, R <sub>2</sub> O–RO–SiO <sub>2</sub> –H <sub>2</sub> O |
| Malolepsy and Petri    | 1986 | Activation of synthetic melilite slags                             |
| Malek. et al.          | 1986 | Slag cement-low level radioactive wastes forms                     |
| Davidovits             | 1987 | Ancient and modern concretes compared                              |
| Deja and Malolepsy     | 1989 | Resistance to chlorides shown                                      |
| Kaushal et al.         | 1989 | Adiabatic cured nuclear wastes forms from alkaline mixtures        |
| Roy and Langton        | 1989 | Ancient concretes analogs  |
| Majundar et al.        | 1989 | C <sub>12</sub> A <sub>7</sub> – slag activation                   |
| Talling and Brandstetr | 1989 | Alkali-activated slag  |
| Wu et al.              | 1990 | Activation of slag cement  |
| Roy et al.             | 1991 | Rapid setting alkali-activated cements                             |
| Roy and Silsbee        | 1992 | Alkali-activated cements: an overview                              |
| Palomo and Glasser     | 1992 | CBC with metakaolin  |
| Roy and Malek          | 1993 | Slag cement  |
| Glukhovskiy            | 1994 | Ancient, modern and future concretes                               |
| Krivenko               | 1994 | Alkaline cements   |
| Wang and Scrivener     | 1995 | Slag and alkali-activated microstructure                           |

His results led him to conclude that alkali hydroxides acted as catalysts, having proved that statement by leaching alkali hydroxides in the same amount as presented in the original mixture. Although the work of Feret [6] may be considered relevant in this field of expertise that work is more about the revision of using blast furnace slag mixed with Portland cement than about alkali-activated binders.

However, it was Glukhovskiy [7] the first author who had investigated the binders used in ancient Roman and Egyptian constructions. He concluded that they were composed of aluminosilicate calcium hydrates similar to the ones of Portland cement and also of crystalline phases of analcite, a natural rock that would explain the durability of those binders. Based on those investigations Glukhovskiy developed a new type of binders that he names as “soil–cement”, the word soil is used because it seemed like a ground rock and the word cement due to its cementitious capacity. The “soil–cement” was obtained from ground aluminosilicate mixed with rich alkalis industrial wastes.

Also Malinowsky [8] had investigated ancient constructions repaired with OPC, having noticed that the repairing material was disintegrated just after 10 years, showing its low durability when compared with the repaired structures. Several authors had reported the existence of almost 40% of analcime zeolites in the composition of mortars found in Jericho in the valley of the Jordan river and also in Tel-Ramad Siria, as old as 7000 B.C. [9–11]. Other researchers had analyzed Roman mortars having also found the presence of analcime [12,13]. Campbell and Folk [14] showed that the durability of ancient binders was due to its high level of amorphous zeolitic compounds. Also Granizo [15] thinks that the presence of zeolitic compounds in several ancient binders suggests they are the final stable phase of a long term conversion of the primary phases to zeolite-like materials.

A large part of the investigations about alkali-activated binders is related to the activation of blast furnace slag, known as “Alkali-slag cement” or “Alkali-activated slag cement”. Blast furnace slag is a by-product of iron production industry, having a high content of calcium which is due to the use of calcium carbonate in the calcination operations. Being a low performance cementitious material, it can achieve high compression strength when an alkaline activator is used. Shi and Day [16] mentioned that the alkali-activation with  $\text{Na}_2\text{O} \cdot n\text{SiO}_3$  led to a compression strength of 160 MPa after 90 days curing at room temperature.

However, Glukhovsky [17] had already made crucial investigations about the activation of blast furnace slag: (a) identifying hydration products as being composed by calcium silicate hydrates and calcium and sodium aluminosilicate hydrates and (b) noticing that clay minerals when submitted to alkali-activation formed aluminium silicate hydrates (zeolite). This author [18] classified the alkaline activators in six groups, where M is an alkali ion:

- (1) Alkalies, MOH.
- (2) Weak acid salts,  $\text{M}_2\text{CO}_3$ ,  $\text{M}_2\text{SO}_3$ ,  $\text{M}_3\text{PO}_4$ , MF.
- (3) Silicates,  $\text{M}_2\text{O} \cdot n\text{SiO}_3$ .
- (4) Aluminates,  $\text{M}_2\text{O} \cdot n\text{Al}_2\text{O}_3$ .
- (5) Aluminosilicates,  $\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot (2-6)\text{SiO}_2$ .
- (6) Strong acid salts,  $\text{M}_2\text{SO}_4$ .

Investigations in the field of alkali activation had an exponential increase after the research results of the French author Davidovits [19] which developed and patented binders obtained from the alkali-activation of metakaolin, having named it after the term “geopolymer” in 1978. According to that author, the new binder is generated by an adjustment of the process used by the Roman and the Egyptians. Davidovits even suggests that the pyramids were not been made with natural stone but were made of man made binders instead. Based on chemical and mineralogical studies he stated that the pyramid blocks were made of a mixture, with limestone sand, calcium hydroxide, sodium carbonate and water. According to his investiga-

tions, pyramid blocks were not made of calcium fossilized layers as it happens in natural stones, but oriented in a random manner as in an artificial binder. XRD diffraction patterns of pyramid specimens indicate that  $(\text{CaCO}_3)$  is the major crystalline phase. However, an amorphous material composed of aluminosilicates and a zeolite like material ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) were also found [20].

For the chemical designation of the geopolymer Davidovits suggests the name “polysialates”, in which Sialate is an abbreviation for aluminosilicate oxide. The sialate network is composed of tetrahedral anions  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$  sharing the oxygen, which need positive ions such as ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{H}_3\text{O}^+$ ) to compensate the electric charge of  $\text{Al}^{3+}$  in tetrahedral coordination (after dehydroxilation the aluminium changes from coordination 6 (octahedral) to coordination 4 (tetrahedral)). The polysialate has the following empiric formulae:

$$\text{M}_n \{-(\text{SiO}_2)_z - \text{AlO}_2\}_n, w\text{H}_2\text{O}$$

where  $n$  is the degree of polymerization,  $z$  is 1, 2 or 3, and M is an alkali cation, such as potassium or sodium, generating different types of poly(sialates) (Fig. 1).

According to Davidovits, geopolymers are polymers because they transform, polymerize and harden at low temperature. But they are also geopolymers, because they are inorganic, hard and stable at high temperature and also non inflammable.

### 3. Terminology

Although these new binders have been named as alkali cements or alkali-activated cements, this name is hardly peaceful, because of the foundings and designations introduced by Davidovits and on the other hand, due to the confusion over the name Portland cement. This binder was overwhelmingly the only one from the last century,

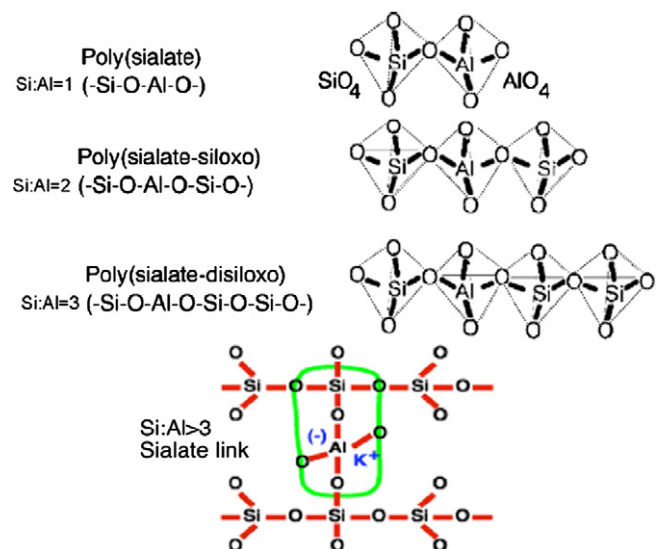


Fig. 1. Poly(sialates) structures according to Davidovits [23].

thus, becoming known as the cement. In fact, Portland cement also hardens in a alkaline environment. The same happens with the pozzolanic reaction, which means that the designation alkaline cement is not very accurate. Davidovits even calls Portland cement as alkali-activated calcium silicates [21].

Over the last few years that author has argued that the designation alkali-activated binders is confusing and may wrongly induce civil engineers. It makes them think it could generate alkali-silica reactions, suggesting other names such as geopolymer cement, geopolymeric cementitious compounds, geocements or poly(sialates) [21–23]. However, although Davidovits has some cause about the ambiguity of the name alkali-activated cement; it is not easy to accept the reason related to the fact that it may mislead engineers about the alkali-silica reaction. Besides, it is not granted that all alkali-activated binders are really geopolymers, nor even clear why some authors mentioned the pozzolanic reaction as being a geopolymeric one [24]. The fact that alkali-activated binders could be considered pozzolanic cements is also raised by other authors [25,26].

According to Palomo, in a conference about geopolymers that took place in 2004 (UTAD-Portugal), the name “geopolymer” is above all a commercial designation and, therefore, should not be used. In fact, the name Portland cement is also a commercial name which is due to the color of the limestone rock from the Dorchester region in England, named as Portland [27]. So it is not very accurate the use of the name Portland cement in other parts of the world as it is the case. That is so due to the importance of the material patented by Aspdin, much more than to any resemblance related to the raw materials used to make Portland cement. Even before the patent of Aspdin in 1824, in 1796 Parker had already patented binders named as roman cements or natural cements [28], using conditions very similar to the ones later involved in the production of Portland cement and, despite that, the work of that author is almost unknown and very rarely mentioned.

So it is believed that the general rule is to use the name alkali-activated binders, and the name geopolymer should only be used when we are really in the presence of a geopolymer, a zeolite with amorphous to semi-crystalline characteristics.

#### 4. Reaction mechanisms

The exact reaction mechanism which explains the setting and hardening of alkali-activated binders is not yet quite understood, although it is thought to be dependent on the prime material as well as on the alkaline activator. According to Glukhovskiy [17], the mechanism of alkali-activation is composed of conjoined reactions of destruction–condensation, that include the destruction of the prime material into low stable structural units, their interaction with coagulation structures and the creation of condensation structures. The first steps consist of a breakdown of the covalent bonds Si–O–Si and Al–O–Si,

which happens when the pH of the alkaline solution raises, so those groups are transformed in a colloid phase. Then an accumulation of the destroyed products occurs, which interacts among them to form a coagulated structure, leading in a third phase to the generation of a condensed structure.

Other authors also agree that the majority of the proposed mechanisms indicate an initial phase of silica dissolution, followed by the phases of transportation and polycondensation [29,30]. However, those phases occur almost simultaneously, preventing their analysis in an individual mode [31]. Granizo [15] studied the alkali-activation of metakaolin having reported different reactions when the alkaline activator is made just of sodium hydroxide or if it also contains waterglass. In the first case, after the dissolution phase an induction period follows, when the destroyed products start to accumulate. In the second case, after a fast dissolution phase a fast polycondensation reaction follows right away. According to Palomo et al. [31], two models of alkali-activation could be established, the first one is the case of the activation of blast furnace slag (Si + Ca) with a mild alkaline solution, having CSH as the main reaction products. In the second model of alkali activation (Si + Al), the general example is the alkali-activation of metakaolin with medium to high alkaline solutions. The final product is characterized by a polymeric model and high mechanical strength. The former model has similarities with the zeolite formation process. Thus, it can be concluded that the activation of metakaolin gives rise to an amorphous polymer just like a zeolite. The alkali activation of fly ashes takes place through an exothermic process of dissolution, during which the breakdown of the covalent bonds Si–O–Si and Al–O–Al occurs. The products generated due to the destruction of fly ash start to accumulate for a period and finally a condensation of the produced structure in a poorly ordered structure with a high mechanical strength.

Other authors [32] believe that the nucleation mechanism involves the ordering of the water molecules by the alkali cations. The lower dimension cations are more fitter than the higher dimension ones. However, in less ordered systems, higher condensations levels have been noticed, as it can be the case of mixtures with more water percentage and less cations to order it, resulting in a higher condensation structure. Alonso and Palomo [33] performed heat evolution tests over sodium hydroxide alkali-activated metakaolin, having identified several phase peaks. A first one due to the dissolution of metakaolin, followed by a induction period with a low heat release and, finally, a third exothermic peak related to the final structure formation and influenced by the concentration of the alkaline activator (Fig. 2).

According to Jaarsveld et al. [34], the geopolymer formation follows the same process of zeolites: (a) dissolution due to the hydroxide ions  $\text{OH}^-$ ; (b) Orientation of the dissolved species; (c) condensation and hardening of the structure in an inorganic polymeric system.



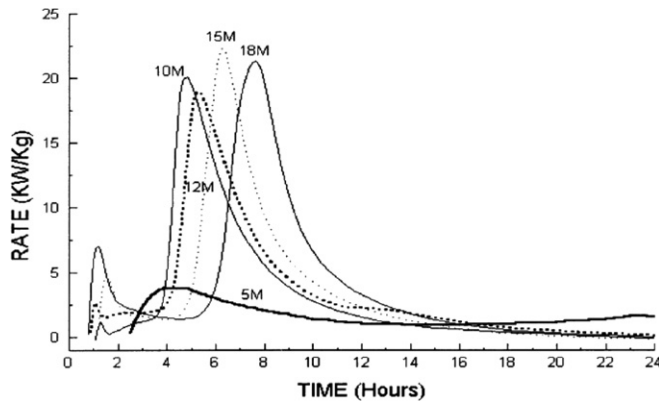


Fig. 2. Heat evolution in samples activated with sodium hydroxide [33].

Krizan and Zivanovic [35] analyzed the heat release in alkali-activated blast furnace slag, and have noticed that the hydration process was influenced by the sodium content and the silica modulus (Ms). The higher  $\text{Na}_2\text{O}$  and Ms were related to higher hydration levels. According to these authors, the process begins with a destruction of the slag bonds Ca–O, Mg–O, Si–O–Si, Al–O–Al and Al–O–Si, related to the initial peaks, and then a second family of peaks occurs due to the formation of a Si–Al layer all over the surface of slag grains and, finally, the formation of the hydration products (Fig. 3).

For Lee and Deventer [36] one of the differences between the OPC binders and the alkali-activated ones is that in the first case it uses water with an initial neutral pH that slowly turns alkaline (12–13) as the hydration process undergoes a series of non-hydrated particles and several types of crystalline CSH gel. In the former case, strong alkali solutions are needed to start the dissolution process. In order to achieve good physical and chemical properties in the final product, it is necessary to add soluble silica (sodium silicate) but, as the initial pH is high, that prevents the coagulation and polymerization of the silicate. When the pH goes to less than 14 due to the dissolution of the prime materials, condensation occurs very quickly. Then a group of reactions of polysialatization, coagulation, colloid formation and hardening occurs in a final product of undissolved aluminosilicate species in an amorphous aluminosilicate structure.

Xu et al. [37] studied mixtures of kaolin, sodium and potassium feldspars activated with waterglass, and reported that the geopolymerization is a three step process: dissolution of kaolin and feldspars forming a gel, condensation of the gel with the polymerization of Al and Si in three-dimensional structures in which the alkali metals compensate the electric charge of the aluminium. During the geopolymerization water acts as a reagent and also as a reaction process. The dissolution phase of Al–Si uses water, but the polymerization releases water. According to Fernandez-Jimenez et al. [38] when the fly ashes are submitted to the alkaline solution, a dissolution process of the Al and Si occurs. Then the higher molecules condense in a

gel (polymerization and nucleation) and the alkali attack opens the spheres exposing small spheres on the inside which will be also dissolved until the spheres, became almost dissolved with the formation of reaction products inside and outside the sphere (Figs. 4 and 5). The activation of fly ashes is a process that may be considered as a zeolitization in which the last phase does not occur, since the experimental conditions lead to very fast dissolution and condensation reactions but a lower one when the hardening take place [39].

For Criado et al. [40], the activation of fly ashes is a process very different from the Portland cement hydration, but resembling the chemical principles involved in the formation of several types of zeolites with an alkaline aluminosilicate as the main reaction product. This reaction product involves the tetrahedral coordination of silica and aluminium in polymeric chains in which the  $\text{Al}^{3+}$  replace the  $\text{Si}^{4+}$ , with the negative electric charge being compensated by alkali cations. During the alkali attack of the aluminosilicate material, an initial nucleation phase takes place where the aluminosilicate species are dissolved. When the nuclei reach a critical size, they start to crystallize, but this is a very slow process so it may only be complete after a long time.

Other authors studied the activation of metakaolin pastes and confirmed that the initial phase formed during the geopolymerization is later transformed to a second, more ordered phase. They noticed however that increasing  $\text{SiO}_2/\text{AlO}_3$  ratio generally decreases the initial rate of reaction [41,42].

Fig. 6 presents a simplified model of the reaction processes involved in the geopolymerization of metakaolin [43]. However, Deventer et al. suggests that it may also apply for other aluminosilicate raw materials. Those authors shows how the presence of calcium and iron influences fly ash geopolymerization kinetics, by providing extra nucleation sites [44].

## 5. Hydration products

As far as the final hydration products are concerned, several authors reported different results to different prime materials. Criado et al. [40] studied the activation of fly ashes having detected with XRD analysis the hydration products hydroxisodalite and herschlite. Shi et al. [45] studied the alkali activation of blast furnace slag, having noticed the formation of CSH and xonotlite. As for Wang and Scrivener [46] they confirmed that CSH gel is the main reaction product of alkali activation of blast furnace slag, having also noticed a low C/S ratio. That is probably due to the high pH solutions, which favors low Ca concentrations and high Si concentrations. These authors reported the formation of hydrotalcite, whenever the alkaline solution was composed just of sodium hydroxide or mixed with waterglass. They did not found any kind of zeolitic phases, or from the mica group containing alkali cations.

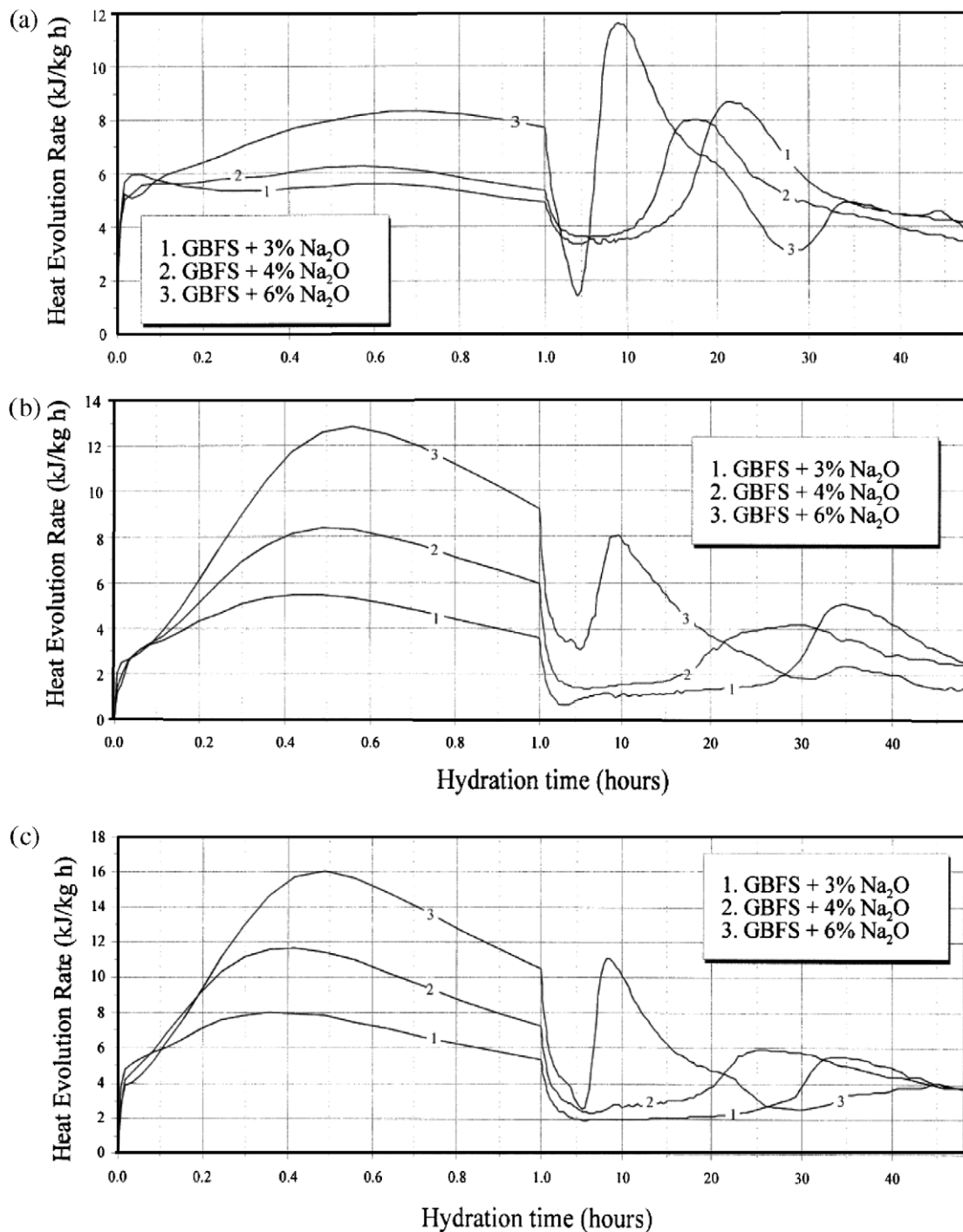


Fig. 3. Heat evolution in alkali-activated slag: (a) silica modulus  $M_s = 0.6$ ; (b)  $M_s = 1.2$ ; (c)  $M_s = 1.5$  [35].

Brough et al. [47] detected high amounts of zeolitic phases (tobermorite, hydroxysodalite) and Na-PI (gismondite) which maybe due to the high water/binder ratio ( $W/B = 1$ ), because water excess is a crucial aspect in the crystallization of  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  and  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  systems.

Some researchers [48,49] mentioned not to have found sodium based hydrated compounds (zeolites), but stated that the most likely that sodium was inside the CSH gel, which can be confirmed by the low C/S ratio, meaning

replacement of the ion  $\text{Na}^+$  by  $\text{Ca}^{2+}$ . This explanation is also stated by Gifford and Gillot [50]. Other authors [51–53] even demonstrated that the amount of sodium inside the CSH phase increases with the decrease of C/S ratio. Sometimes the sodium amount is higher enough so the gel is named as NCSH [51,54].

Palomo et al. [31] did not find any new crystalline phases except the already existing in the original fly ashes. These authors noticed that when the activator is made of water-glass and NaOH the Si/Al ratio doubles, although the

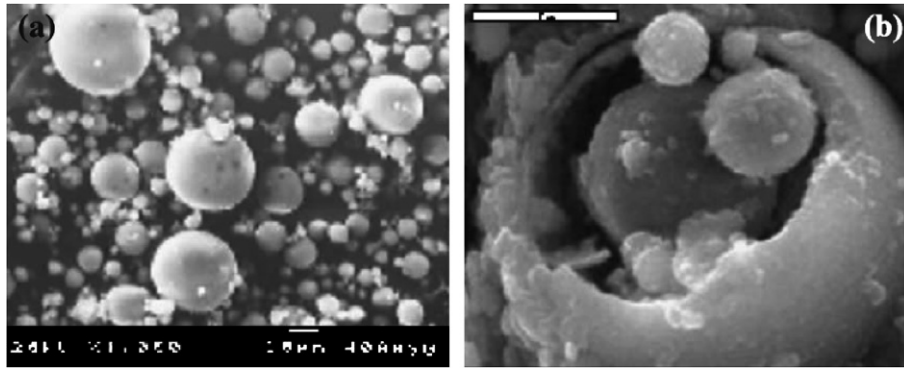


Fig. 4. Microstructure of alkali activation of fly ash: (a) original fly ash spheres; (b) broken spheres after activated with sodium hydroxide [38].

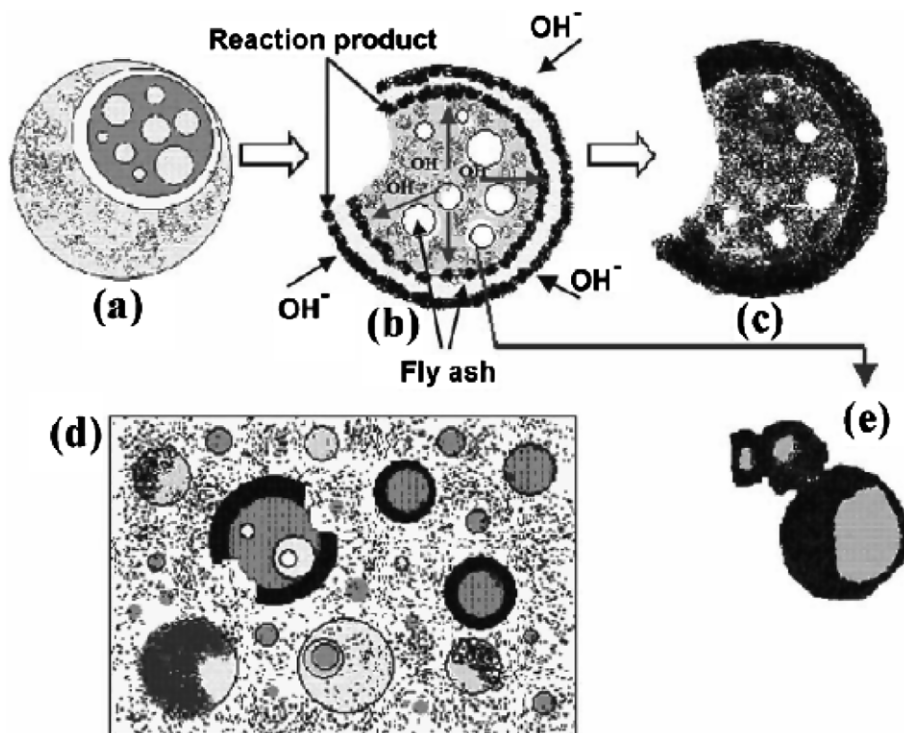


Fig. 5. Descriptive model of the alkali activation of fly ash [38].

Na/Al ratio remains the same. For the hydration products they reported the following ratios: (Si/Al = 2.8; Na/Al = 0.46 for an activator made of NaOH) and (Si/Al = 5.2; Na/Al = 0.46 for an activator made of NaOH mixed with waterglass).

Puertas et al. [55] studied mixtures of fly ashes and blast furnace slag, having reported that CSH gel was the main reaction product, they also detected the formation of hydrotalcite ( $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ ), pirssonite ( $\text{Na}_2\text{Ca}(\text{CO}_3) \cdot 2\text{H}_2\text{O}$ ), as well as calcite, however, they did not find any alkaline aluminosilicate phase.

According to Fernandez-Jimenez and Palomo [56], the XRD patterns of alkali-activated fly ashes show that the original crystalline phases are not changed by the activation reactions. Some peaks related to quartz appear with

more intensity, which as they explain is due to a possible sand particle that was left in the sample. These authors found zeolitic phases in the XRD patterns such as hydroxysodalite ( $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{OH}$ ) and herschelite ( $\text{NaAl-Si}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$ ). The SEM analysis showed that, before the activation, the fly ashes are composed of spheres of different sizes with some crystals of mullite and iron. After the activation, the SEM analysis shows some unreacted spheres and aluminosilicate gel with the molar ratios (Si/Al: 1.6–1.8) and (Na/Al: 0.46–0.68) for mortars activated only with NaOH. When the activator contains also waterglass the final product is more compact, with the following molar ratios (Si/Al: 2.7) and (Na/Al: 1.5).

Phair and Deventer [57] indicate that the dissolution of Si and Al species from metakaolin is high for pH 12.

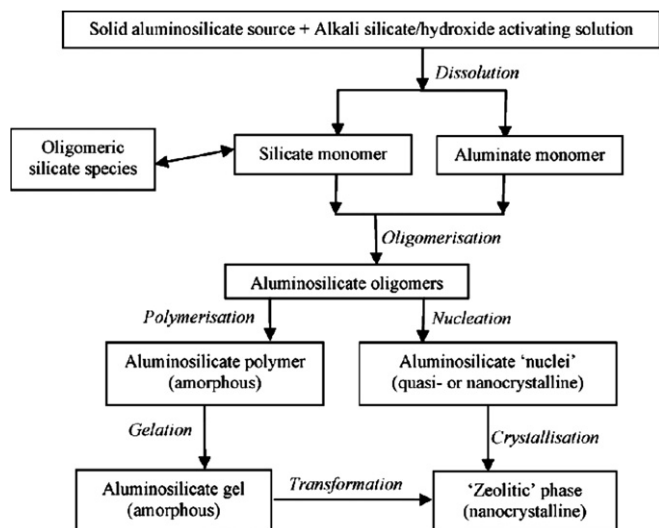


Fig. 6. Schematic outline of the reaction processes involved in geopolymerization [43].

However, for those conditions, Na, Ca and Mg have almost no dissolution. Compared to kaolin, the aluminium dissolution is 10 times higher and the silica dissolution is two times higher. As for Na, Mg and Ca its dissolution is lower in the metakaolin.

Xie and Xi [58] studied the alkali activation of fly ashes with NaOH mixed with waterglass, and noticed that, for the SEM analysis, a large amount of crystals was detected due to unreacted waterglass which had crystallized. As for the XRD analysis, only the characteristics peaks of the original fly ashes were detected among a few small reaction products peaks. Krivenko and Kovalchuk [59], for the alkali activation of fly ashes with NaOH and waterglass also reported the formation of zeolites like analcime and hydroxysodalite with high molar ratios,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (4.5–5). Zhuhua et al. [60,61] studied the alkali activation of blast furnace slag mixed with red mud, having noticed that the hydration products are CSH with a molar ratio, Ca/Si (0.8–1.2). They did not detect any zeolitic phase or even portlandite. Brough and Atkinson [62] also studied the activation of blast furnace slag, and reported that XRD analysis shows no crystalline products, however, the SEM analysis reveal the formation of hydrotalcite after a month.

Other authors [63] studied blast furnace slag mortars with 10% replacement by silica wastes silica, obtaining CSH gel and hydrotalcite as reaction products. Puertas and Fernandez-Jimenez [64] analyzed alkali-activated mixtures of blast furnace slag and fly ashes in a percentage of 50%, and reported two types of hydration products: CSH gel Ca/Si = 0.8; Al/Ca = 0.6; Si/Al = (2–3), a calcium silicate hydrate aluminium with sodium in its structure and also an alkaline aluminosilicate hydrate with a three-dimensional structure due to the fly ash activation.

As for Song et al. [65] the main reaction product of blast furnace slag hydration is CSH gel with minor amounts of hydrotalcite, that was detected by XRD analysis, which

are formed only when the slag achieves a high level of hydration [66].

Puertas et al. [67] studied blast furnace slag activated with NaOH, and has reported by XRD analysis the presence of hydrotalcite ( $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ ), calcite ( $\text{CaCO}_3$ ) and CSH. Those authors have noticed that when using the activator NaOH, it leads to reaction products with the molar ratio Al/Si higher than the one obtained with the activator NaOH mixed with waterglass. Their explanation has to do with the replacement of Si by Al in the tetrahedral location of the silicate chain. For the two activators the following molar ratios were obtained:

- (a) NaOH: Ca/Si (0.9); Al/Ca (0.4); Mg/Ca (0.5–0.6); Al/Si (0.4); Na/Al (0.8–0.9).
- (b) NaOH mixed with waterglass: Ca/Si (0.3–0.4); Mg/Ca (0.4–0.7); Al/Si (0.2–0.3); Na/Al (0.3–1.8).

Other authors used metakaolin activated with NaOH mixed with waterglass, and reported an amorphous phase and also a crystalline one (quartz and mullite unreacted) in the XRD analysis. They also noticed that increasing sodium hydroxide concentration led to an increase of the amorphous phase. As for the microstructure analysis they found that the hardened material kept the same layered structure typical of metakaolin [68].

De Silva et al. [69] reported that high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  metakaolin mixtures resulted in amorphous Na–Al–Si containing polymer phases (geopolymer), but they did not found enough evidence to confirm any amorphous to crystalline transition associated with the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, as reported by Fletcher et al. [70].

## 6. Conclusions

The development of alkali-activated binders seems to present a greener alternative to OPC. This paper reviews his historical background, terminology, reaction mechanisms and hydration products. From the review, it can be concluded that an extensive research has already been carried out. The right name for these binders is alkali-activated binders for the general case although the term “geopolymer” is accepted in some cases. The exact reaction mechanism of alkali-activated binders is not yet quite understood, although it depends on the prime materials and on the alkaline activator. Despite that, most authors agree it consists in a three step model of dissolution, orientation and hardening. The reaction products depend also on the activator and on the prime materials, and the systems (Si + Ca) have a CSH gel as the main reaction product. As for the systems (Si + Al) the reaction products are zeolite like polymers.

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