Usage of supplementary cementitious materials: advantages and limitations

Part I. C–S–H, C–A–S–H and other products formed in different binding mixtures

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Abstract

It is well known that cement production is not neutral for natural environment among others due to high CO₂ emission. Different strategies of mitigation of negative environmental impact of its production are developed. One of the ways is utilization of supplementary cementitious materials (SCMs) in the manufacture of cement and concrete. Introduction of aluminosilicate SCMs into binding mixture makes that more amount of so-called C–A–S–H phase appears in hydration products, affecting microstructure and properties of final hardened composite. The aim of this work is to discuss the possibilities of utilization of selected SCMs in different binding mixtures including some advantages and limitations. Literature review on the subject was carried out. Some of our own research results were also presented. In the Part I of this review, some information about history of ancient binding materials and the possibilities of inspiring modern engineers with ancient constructions in the aspect of using SCMs in modern concrete were presented. Using pozzolanic aluminosilicate SCMs in relation to their influence on formed products, microstructure and mechanical properties of hardened material were discussed. Some problems with possibilities of study of SCMs reaction degree were identified. Emphasis was put on the usefulness of isothermal calorimetry and thermal analysis for investigations of hydration process and identification of hydrated products as well as evaluation of degree of reaction of SCMs.

Keywords Supplementary cementitious materials · Cement · Blended cement · Pozzolana · Hydration · Thermal analysis

Introduction

Cement and cement concrete are common construction materials manufactured in large amounts. The demand for cement has been increasing for many years which is an effect of global urbanization. For example, during the decade between 2004 and 2014 above 90% increase in worldwide cement production was observed. After 2014, some stagnation in cement manufacture takes place [1]. In 2017, the cement world production was above 4 Gt/year [1, 2]; however, further growth is expected in the coming years. China

produced and consumed the most amount of cement; it is above 50% of total worldwide production [1–4].

Unfortunately, production of cement clinker is not neutral for environment as it consumes large amount of energy and natural resources and causes emission of CO₂ which is estimated as 5–8% of the annual worldwide CO₂ emissions from anthropogenic sources [3–7] (about 842 kg CO₂ per tonne of clinker [3, 8], 600–700 kg CO₂ per tonne of cement [3]). The greenhouse gas emission covers mainly CO₂ arising from high-temperature decomposition processes taking place during cement clinker production. It amounts to 50–60% of CO₂ generated during cement manufacture. Combustion of fuels is in second place (about 40% of CO₂ emission) [1, 4, 6–8]. Then, with smaller amount, electricity and transport contribute to CO₂ emission [3, 4, 6, 7].

Due to the significant demand for cement and the need to reduce anthropogenic CO₂ emissions, different strategies of mitigation of negative environmental impact of cement

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Fig. 1 The main groups of silica and aluminosilicate SCMs that can be used in cement composite

production are developed. They cover activities related to reduction of CO_2 emission in the four, mentioned above, problematic fields, i.e. decarbonation process during clinker production, combustion of fuels, transport and electricity. The main directions of such activities are as follows [3–5, 8–10]: modification of cement production technology, using alternative fuels, using alternative raw materials for the production of clinker and supplementary cementitious materials (SCMs) as cement/clinker replacements, development of new more ecologically friendly cements and clinkers (alkali-activated binders including geopolymers, belite-rich Portland clinkers, belite-Ye'elimite-Ferrite clinkers, carbonatable calcium silicate clinkers, magnesium-based concretes, etc.) and other. Capture and storage of CO_2 is also proposed [3, 6, 8]. Some of the concepts are not developed enough and require further in-depth research.

Reduction of CO_2 emission from the high-temperature limestone decarbonation process is of a special challenge. Firstly, because this kind of emission is responsible for about 60% of total CO_2 emission resulting from cement production and secondly because decarbonation processes are the base of creation of substrates necessary for the formation of cement clinker minerals. Reduction of limestone calcination will result in change of the composition of the final cementitious material [8]. For this reason it is not easy to reduce this emission of CO_2 .

One of the ways, as it was indicated in this work earlier, is utilization of SCMs in the manufacture of cement and concrete. Different fine-grained silica, silicate and aluminosilicate materials of natural or artificial origin can be used in cement composites giving possibilities to obtain a new ecologically friendly cementitious binder of modified properties. The most commonly used SCMs are as follows [8]: fly ash, silica fume, granulated blast furnace slag, metakaolin, natural pozzolana, limestone. Most of them are industrial by-products which require utilization.

It is commonly accepted that aluminosilicate and silica SCMs may be divided into three main groups (Fig. 1) depending on their chemical and phase composition and resulting from these reactivity in hydrating cement system. They are: pozzolanic materials, hydraulic materials and materials being inactive or showing only small reactivity in cement system [11, 12]. In this work, the attention was mainly devoted to the first of these groups of materials, i.e. pozzolans. They can be used as components of commercially available cements (e.g. in the case of CEM II according to [13]) or additive to cement concrete (e.g. fly ash according to [14]). Current trends in cement development cover multicomponent binders, i.e. cement or cement clinker plus different (at least two) SCMs [10, 15–21]. Such ternary or even four-component binders give possibility to improve properties of binary blends by synergistic effect.

The aim and scope of the work

The aim of this work is to discuss the possibilities of utilization of selected SCMs in different binding mixtures. Mechanisms of hydration processes depending on various factors were discussed because kinetics of these processes and kinds of solid products that are formed influence properties of final composites. Moreover, knowledge about chemical and physical processes taking place in hardening binder gives possibility to develop new more advanced blends which can replace cement. The discussion was carried out mainly based on the literature review on the subject but also on our own research results including not yet published ones.

In the Part I of this review, usage of aluminosilicate SCMs in relation to their influence on hydration processes, formed products, structure of hardened material and mechanical properties were discussed. The possibilities of inspiring modern engineers with ancient constructions in the aspect of using SCMs in ecological high-performance concrete were presented. Emphasis was put on the usefulness of isothermal calorimetry and thermal analysis for such investigations, especially in the case of evaluation of degree of reaction of SCMs.

Pozzolanic reaction: reactivity of SCMs and the ways to study it

Fine-grained SCMs containing active forms of silica or alumina when introduced into cement mixture can react with $\text{Ca}(\text{OH})_2$ which is formed during cement hydration [11]. As a result, additional amount of C–S–H¹ and C–A–S–H phases are formed while $\text{Ca}(\text{OH})_2$ content is reduced. As it has already been mentioned above (Fig. 1), such kind of SCMs, i.e. containing low calcium components and not showing self-cementing properties but being able to react with $\text{Ca}(\text{OH})_2$ in the presence of water, are commonly known as pozzolana (pozzolanic materials/additives).

The increasing use of aluminosilicate SCMs in cement composites means that the binding mixture can contain higher amount of aluminium compounds and, in consequence, lower amount of calcium in comparison with typical Portland cement. It causes that C–S–H formed in such mix has lower C/S ratio [11, 22–26] compared to product formed during hydration of Portland cement without SCMs. In cement-SCMs composite, the basic properties, such as compressive strength, durability, tightness, etc., are mainly

shaped not only by C–S–H phase, as in the case of neat Portland cement, but also by C–A–S–H. Its influence depends on C–A–S–H amount and morphology.

Possibilities to use different SCMs in cement-containing binders depend on SCMs properties and availability. In general, aluminosilicate SCMs can be used in different amounts in binding composite starting from low and ending on very high or even 100% cement replacement (no-clinker binders). For small or moderate amount of SCM in cement binder, compressive strength of cement composite can be improved because of pozzolanic reaction and, in case of very fine grains of SCM, acceleration of cement hydration by nucleation action [11, 27, 28]. Reactivity of SCMs is often lower than reactivity of clinker phases [22], which causes that for high and very high cement replacement level, pozzolanic reaction and acceleration of cement hydration may be insufficient to obtain required properties of final composite. In such case different ways of activation of the system and increasing of SCM reactivity are considered [29].

Several factors influence reactivity of SCM, such as chemical and phase composition of SCM, morphology of its grains (size of grains and their shape, specific surface area), level of cement substitution, conditions of hardening (e.g. pH of reaction media, temperature), type of cement used. Reactivity of SCMs is crucial for development of properties of final composite. Thus, investigation concerning hydration processes taking place in binders of new compositions is important not only from a scientific but also from a practical point of view. Calorimetry and thermal analysis are commonly used for such testing.

Calorimetry uses the fact that cement hydration and pozzolanic reaction are exothermic. The method is very useful in studies of early hydration periods when physicochemical processes occur at the fastest rate. Isothermal calorimetry allows to continuously record the heat emitted from the moment of adding water to the binder. Heat release is directly related to the physicochemical processes taking place in the reacting system. This is why, shapes of the recorded curves correlate very well with the appearance of hydrated phases and they help to estimate some properties of the mixture. General shape of calorimetric curve showing early cement hydration is well-known and its description can be found in numerous publications, e.g. [11, 28, 30–34]. They show that typical calorimetric curve for cement paste can be divided into five periods which are marked in Fig. 2. There are: (1) initial (wetting) period taking place short after addition of water, (2) induction period, (3) acceleration period, (4) deceleration period (after final setting time, cement paste has solid structure), (5) stage of slow continued reaction (growing of hydration products and thickening of the structure, reactions are diffusion-limited). Additional effect of heat release which can be observed for some samples at the falling curve in the 4th

¹ C–S–H—calcium silicate hydrate of low crystallinity and different composition, according to abbreviations used in cement chemistry: C–CaO, S–SiO₂, H–H₂O; other abbreviations used in cement chemistry: A–Al₂O₃, N–Na₂O, F–Fe₂O₃.

Fig. 2 Exemplary results of cumulative heat released (a) and heat release rate (b) for selected commercially available cements, 1–5: explanation in the text (water-to-cement ratio was 0.5, BMR calorimeter (Institute of Physical Chemistry, Polish Academy of Sciences) was used, the results were calculated using computer software [35])

period is often interpreted as “aluminate peak” showing sulfoaluminate crystallization or hydration of aluminates after gypsum depletion.

The presence of SCMs in the binder usually changes the kinetics of heat release. For example, calorimetric results presenting an influence of the amount and kind of fly ash on cement hydration can be found in [29]. In the case of cement-SCMs paste, hydration heat evolution depends on: the kind of cement (phase composition), the kind of SCM, the amount of water, presence of admixtures, temperature. Synergic effects may take place in the system—components of SCM-cement paste can influence reactivity of each other. Figure 2 presents examples of calorimetric curves registered for commercially available cements containing SCMs: CEM II/B-V 32.5 N (cement-containing Class F fly ash in an amount of 21–35% [13]) and CEM III/A 42.5 N (cement-containing granulated blast furnace slag in an amount of 36–65% [13]). Heat release curve and cumulative heat for Portland cement CEM I 32.5R (reference paste) were also presented. The results confirm lower exothermicity of cements with reduced Portland clinker amount compared to the result for neat cement. Additional thermal effect visible at about 24 h for CEM III-paste may indicate hydration of granulated blast furnace slag which has so-called latent hydraulic properties.

It should be noted, however, that studying mechanism of reactions occurring in cement-SCM system, using only calorimetry, is an insufficient method despite many of its advantages. Thus, other complementary methods are needed. Following techniques can be useful to investigate early hydration and hardening periods when chemical processes go with the highest rate: conductivity, ultrasonic wave measurements, setting time. They allow measurements to be made continuously from the moment of adding water to the binder.

Thermal analysis is mostly used in the case of hardened binder; thus, it is a useful method of investigation of later hydration periods to identify the obtained products. It is based on the fact that components of cement paste can dehydrate or decompose under raising temperature. In this way the amount of water bound in hydrates and the content of $Ca(OH)_2$ can be estimated. Exemplary TG/DTG/DTA curves for the same cement pastes as described above as well as for mix of cement and fly ash are presented in Figs. 3 and 4. Figure 3 depicts TG/DTG/DTA curves for cement paste containing 25 mass% of fly ash from pulverized combustion of brown coal (water/(cement + fly ash)=0.5). The chemical composition [mass%] and phase composition of this fly ash were as follows: SiO_2 61.7%, Al_2O_3 11.3%, Fe_2O_3 2.7%, CaO 17.1%, SO_3 1.7%, $Na_2O + K_2O < 0.5\%$, MgO 1%, crystalline components (detected in X-ray diffraction patterns): quartz, anhydrite, anorthite, gehlenite, haematite, calcite, free CaO [29]. Figure 4 shows TG and DTG curves for different kinds of cement (CEM I, CEM II and CEM III) for a comparison. The curves have shapes typical for cement pastes, i.e. three main endothermic mass losses. Their general interpretation is given in Fig. 3, and it agrees with well-known interpretation of TG/DTG/DTA results for cement paste, e.g. [18, 20, 21, 29]. The interpretation can be confirmed by TG/EGA measurements which exemplary results are presented in Fig. 5. EGA curves show that, during heating of hardened cement paste, water is mainly released till 500 °C, while at higher temperature CO_2 appears in gas products of thermal decomposition. It is visible that cement-fly ash paste and CEM II-paste (Figs. 3 and 4) have lower amount of water bound in hydrates and lower content of $Ca(OH)_2$ compared to result for reference paste. It is an effect of cement clinker reduction and pozzolanic reaction. Lower amount of $Ca(OH)_2$ is also visible in the case of CEM III-paste while the amount of bound water is similar to the result for reference sample. It may indicate that hydrates of different compositions (various C/S and A/S ratio and water content) are formed depending on sample composition.

Other methods that are widely used in testing hardened cement materials are: X-ray diffraction, NMR, SEM, FTIR, etc.

It is a very important problem but also necessity to develop precise and reliable techniques enabling quantitative

Fig. 3 Exemplary results of TG, DTG and DTA curves for cement paste containing 25% of fly ash (25% FA + 75% PC) and reference cement paste (100% PC) after 3rd and 28th day of hydration (water/(cement + fly ash) = 0.5, curing at room temperature, hydration was stopped before the measurements by the use of acetone, SDT 2960 Thermoanalyser (TA Instruments) was used, heating rate was 10 °C min⁻¹, nitrogen atmosphere)

determination of the ratio of SCMs reaction in the binder. There are some possibilities, including usage of calorimetric and thermal analysis methods, which are presented in Tables 1 and 2. However, each of these techniques has in addition to the advantages also some drawbacks and limitations. It happens because studied system is multicomponent and difficult for detailed investigation. Different chemical processes occur in parallel, and it is often difficult to

separate those resulting from SCM reactions from processes of cement hydration. In addition, different ingredients affect each other modifying their reactivity. Used procedure of cement hydration inhibition also can affect the results. All this makes that different values of SCM reactivity can be obtained by different methods. The search for a correlation between these results is the appropriate approach. Precision of the method is very important; however, availability of the equipment, cost and time of the analysis as well as ease of interpretation of the results are also taken into account when choosing a method to determine the degree of SCM reaction.

In general, the methods used for estimation of reaction degree of SCM can be divided into two groups: direct and indirect. The first one means techniques which allow to evaluate degree of SCM reaction directly, basing on measurement of the amount of unreacted SCM. Indirect methods are based on measuring some properties of sample (e.g. the amount of $\text{Ca}(\text{OH})_2$ consumed in pozzolanic reaction or compressive strength of hardened material) which depend on SCM reactivity [27]. Then degree of SCM reaction is calculated, often as a ratio of the measured quantity to the result for fully reacted SCM.

Thermal analysis and calorimetry are often used indirect methods. Cumulative heat released during hydration, an amount of bound water and $\text{Ca}(\text{OH})_2$ are determined and related to SCM reactivity. Techniques that enable quick obtaining of the results and relating them to the properties of the hardened material are particularly valuable. In this way it is possible to predict the long-term properties of the composite in terms of its durability and strength. Calorimetry is one of such methods that gives results relatively quickly. Problem of determination of SCMs reaction ratio has not been fully resolved until now and needs further research.

A few words about history of ancient binding materials

Portland cement was invented in the nineteenth century. Thus, it is a relatively young binding material taking into account that the oldest evidence of the use of mortar or concrete with lime binder dates back to the year 7000 B.C. [54, 55]. However, the invention and dissemination of concrete, i.e. hard material similar to natural stone, are attributed to the ancient Romans. They used lime mortar and volcanic tuff commonly found in Mediterranean areas [11, 54–59]. In this way, hydraulic binder which undergoes hardening in the presence of water was invented. This material developed very good functional properties as a result of long-term chemical and physical processes taking place in the structure. Generally speaking, active silica and alumina coming from tuff reacted with $\text{Ca}(\text{OH})_2$ resulting in the formation of hydrated aluminosilicate phases which

Fig. 4 Exemplary results of TG and DTG curves for cement pastes performed with selected commercially available cements after 1st and 28th day of hydration (water/cement=0.5, curing at room tem-

perature, the same methods and apparatus were used as in the case of results presented in Fig. 3)

provided hardening of the material and development of its strength and durability. Tuff from Puccoli (Puteoli) near Naples exhibited very good reactivity [11, 54, 55, 57, 60] (this is why, nowadays, similar silica and aluminosilicate materials which are able to react with $\text{Ca}(\text{OH})_2$ in the presence of water are named pozzolana or pozzolanic materials (pozzolanic additives) and the reaction—pozzolanic reaction). Some artificial materials, such as ground ceramics, were also used [11, 55, 57, 58, 61]. Lime which did not

undergo pozzolanic reaction was carbonized with atmospheric CO_2 .

Romans' mastery of concrete production based on a lime binder with volcanic tuff makes it possible today to admire the many ancient buildings, including aqueducts, roads but also monumental constructions. One of examples of excellent ancient constructions is, built between 118 and 128 AD, the Roman Pantheon (Fig. 6a) which walls are made of bricks, but the concrete was used in foundations and

Fig. 5 Exemplary TG/EGA curves for hardened cement paste (water/cement=0.5, curing at room temperature, hydration was stopped before the measurements by the use of acetone, SDT 2960 Thermoanalyser (TA Instruments) coupled with mass spectrometer QMS ThermoStar (BALZERS) were used, heating rate was $10\text{ }^{\circ}\text{C min}^{-1}$, helium atmosphere)

the huge dome [54]. The dome structure which is 43.3 m in diameter and has a round hole on the top is particularly admirable. Another example of a remarkable huge Roman construction is the Colosseum (70–82 AD, Fig. 6b), in which bricks and large amounts of concrete were used to construct vaults and internal walls while the outer walls are made of travertine and bricks [54].

When considering durability of ancient Roman constructions, a few questions appear. Could the ancient constructions be or not an inspiration for modern building industry engineers to project ecological high-performance concrete? What was the concrete mix design in those days and what is currently the composition of hardened ancient binders? The answers to some of the questions are possible to obtain by modern studies of samples collected from ancient concrete. Thermal analysis, as complementary research method, finds application in this type of investigation, enabling the estimation of some components, like calcium–aluminium–silicate–hydrate (C–A–S–H) or carbonates. For example, Silva et al. [60] found that Colosseum mortar is mainly composed with calcite which was evidenced in TG/DTA results as significant endothermic mass loss at temperatures 600–750 $^{\circ}\text{C}$. Presence of some amount of amorphous aluminosilicate hydrates (not detectable in XRD analysis) was not excluded

as continuous mass loss (about 15%) at temperature range up to about 600 $^{\circ}\text{C}$ was also observed [60]. Similarly, TG/DTG results for samples of lime mortars from the Ponte di Augusto Roman bridge also show that this mortar is mainly composed of carbonates as indicated by significant mass loss connected with their thermal decomposition [62]. Moreover, mass loss related to evaporation of bound water indicates presence of hydrated silicates and aluminates which formed as products of a pozzolanic reaction [62]. Borosoi et al. [61] investigated samples of mortar coming from the roman archaeological site of Pisões (Portugal) by the use of thermal analysis as one of research methods. They, similarly as authors which research results are presented above, also found calcite and pozzolanic reaction products such as C–S–H and C–A–H in investigated materials (effects on TG/DTA curves at 600–900 $^{\circ}\text{C}$ and 200–600 $^{\circ}\text{C}$, respectively, the latter one may also be an effect of dehydration of water chemically bound in clay minerals). Moreover, in some samples, authors of [61] identified calcium monocarboaluminate (peak at about 220 $^{\circ}\text{C}$) and MgCO_3 (decomposition at 450–550 $^{\circ}\text{C}$). Other examples of the use of thermal analysis as a complementary method to the study of Roman mortars and other historic buildings can be found in [63–68]. Thermal analysis is also applicable in investigation of today produced natural pozzolan–lime pastes to provide, e.g. relevant information useful in the restoration interventions of historic buildings [69].

Exemplary results of our investigations of present-day performed samples of fly ash–lime binders are presented in Figs. 7 and 8 which show TG/DTG/DTA curves and IR spectra, respectively. The compositions of investigated mixtures can be considered as similar, to some degree, to ancient natural pozzolan–lime binders. The samples, investigated by us, were prepared with $\text{Ca}(\text{OH})_2$ (30 mass%), fly ash² (70 mass%) and distilled water (water to solid mass ratio was 0.5). Na_2SO_4 of analytical purity was also added in an amount of 4 mass% calculated in relation to the mass of fly ash + $\text{Ca}(\text{OH})_2$. After mixing, the pastes were poured into small plastic moulds (capacity of 25 cm^3), and then they were divided into two groups and stored under different conditions: at room temperature at laboratory conditions and at 45 $^{\circ}\text{C}$ and 95% humidity. Elevated temperature of sample storage may simulate the situation in which temperature of pozzolan–lime mixture with water is rising as a result of exothermic hydration of lime. Such phenomenon could have taken place in ancient concrete because of exothermic

² The main properties of this fly ash (from conventional combustion of hard coal) were as follows: average chemical composition (in mass%): SiO_2 54.2, Al_2O_3 28.9, Fe_2O_3 5.2, CaO 2.3, SO_3 0.2, MgO 1.1, $\text{Na}_2\text{O} + \text{K}_2\text{O}$ 2.6; the main crystalline components were quartz and mullite; the grain shape was mainly spherical; mean grain diameter was 64 μm [29, 70].

Table 1 Research methods used for testing the degree of SCMs reaction in SCM-cement system—determination by the use of thermal analysis and calorimetry

Method	Basis of determination	Benefits and disadvantages, other comments	References
TG, DTG, DTA, DSC	Estimation of $\text{Ca}(\text{OH})_2$ content basing on mass loss or thermal effect of its decomposition	<ul style="list-style-type: none"> indirect method* reduction of $\text{Ca}(\text{OH})_2$ in cement-SCM system or lime-SCM indicates pozzolanic reaction, consumption of $\text{Ca}(\text{OH})_2$ can be calculated – evaluation of pozzolanicity of the SCM calculation of the degree of SCM reaction can be done, e.g. as the ratio of calcium hydroxide consumption in cementitious paste and in $\text{Ca}(\text{OH})_2$ mix (detailed procedure was described in [36]) temperature in which $\text{Ca}(\text{OH})_2$ undergoes decomposition varies depending on e.g. the presence of alkalis quantitative determination of the fraction of SCM reacted can be fraught with error (in early hydration periods – acceleration of cement hydration by fine grains of SCM, at later periods of hydration – carbonation of $\text{Ca}(\text{OH})_2$) negative value of consumed $\text{Ca}(\text{OH})_2$ indicates acceleration of cement hydration by fine SCM (cement hydration predominates over pozzolanic reaction) the fact that SCM can consume Ca not only from $\text{Ca}(\text{OH})_2$ but also from C-S-H formed during cement hydration is neglected, thus real degree of SCM reaction may be higher than the degree calculated based on $\text{Ca}(\text{OH})_2$ reduction 	[15, 22, 27, 36–39, 40]
TG	Determination of water bound in hydrates	<ul style="list-style-type: none"> indirect method estimation of cement reaction degree often bases on comparison of the result for the paste at given hydration time and for a fully hydrated sample the need to know the value of maximum chemically bound water which may be significantly different for blended cements containing various SCMs detailed methodologies including calculation equations and adopted models are different from one author to another, different limits of temperature to determine content of water bound in hydrates (non-evaporable water) can be found in the literature C-S-H, C-A-S-H are the main products of hydration and pozzolanic reaction - stoichiometry of the reactions is not precisely known, hydrates can have different C/S ratio and content of water in the case of SCM-cement paste compared to products of neat cement hydration it is impossible to separate the amount of water coming from products of SCM reaction and from products of cement hydration the way of removing unbound water (inhibition of hydration) influences results of bound water 	[22, 27, 41–45]
DTA, DSC	Determination of exothermic peaks of recrystallization of glass in unreacted SCM	<ul style="list-style-type: none"> qualitative rather than quantitative study relatively large error is possible (different peaks may overlap) 	[41]
Calorimetric measurements of heat release in hydrating blended	Continuous monitoring (usually till 48h) of heat evolved by SCM-cement	<ul style="list-style-type: none"> indirect method comparative investigation of system containing SCM and the one containing the same amount of inert filler (with similar granulation as that of SCM) can be used to attempt to separate chemical and physical influence of SCM on cement hydration 	[15, 36, 41, 42, 44, 46]

Table 1 (continued)

cement paste	paste compared often to results for cement blended with the same amount of inactive filler	<ul style="list-style-type: none"> • calculation of the degree of SCM reaction can be done, e.g. as the ratio of heat released in cementitious paste and in $\text{Ca}(\text{OH})_2$ mix (detailed procedure was described in [36]) • calculation of SCM contribution to the heat flow (i.e. heat flow due to pozzolanicity of SCM) can be made [15]
Calorimetric measurements and thermal analysis of mix of SCM with calcium hydroxide	Heat release measurement in conjunction to determination of $\text{Ca}(\text{OH})_2$ consumption	<ul style="list-style-type: none"> • conditions of the measurements: elevated temperature, KOH presence [47] • evaluation of pozzolanicity of SCMs - distinguishing the SCM as inert, pozzolanic, highly pozzolanic and hydraulic based on plotting the heat release results against calcium hydroxide consumed (estimated by thermogravimetric analysis)
Combined use of various methods to study pozzolanic activity and the degree of SCM reaction	Search for correlation between results obtained by various methods	<ul style="list-style-type: none"> • Correlation can be found between: cumulative heat released during given hydration time and compressive strength, bound water and compressive strength, bound water and cumulative heat released [48] • Elevated temperature of sample curing can be used to accelerate the SCM reactivity and to get the results faster

*Direct method—degree of SCM reaction is evaluated based on direct measurement of the amount of unreacted SCM remaining in the system

Indirect method—calculation of degree of reacted SCM based on some other measured quantity [27]

hydration of lime. It should be emphasized that the temperature profile of self-heating mixtures depended on a few factors, such as the amount of lime in the mix, the size of the designed element and possibility of heat release outside. In the case of massive structures, heat can be accumulated resulting in considerable increase in the temperature inside, e.g. in the case of harbour constructions described in further part of this work. General interpretation of the results obtained for fly ash- $\text{Ca}(\text{OH})_2$ pastes is depicted in Figs. 7 and 8. Typical three mass losses are visible on TG curves, similarly as in the case of cement paste. It can be seen that curing temperature and presence of sulphate salt significantly influence the rate of early hydration/pozzolanic processes and formed products. The elevated temperature and presence of Na_2SO_4 favour the increase in reaction degree. It is visible that such sample shows lower amount of $\text{Ca}(\text{OH})_2$ content and bigger amount of water bound in hardened phases type of C-S-H, C-A-S-H and ettringite compared to results for other specimens. The presence of ettringite was confirmed in results of XRD and SEM investigations for similar samples but containing small amount of Portland cement [70]. IR spectra also confirmed lower $\text{Ca}(\text{OH})_2$ content in the samples containing Na_2SO_4 and cured at elevated temperature indicating higher degree of pozzolanic reaction. However, it should be remembered that in such system $\text{Ca}(\text{OH})_2$ may also be involved in ettringite formation in addition to pozzolanic reaction with aluminosilicate grains of fly ash. More clear appearance of binding phases type of C-(A,N)-S-H

is also visible in IR spectra of sample containing Na_2SO_4 and cured at 45 °C, especially after longer hydration time. Thus, presence of Na_2SO_4 admixture and elevated temperature influence the kinds of formed products. Other results of TG/DTG and IR investigations of similar systems can be found in our papers [70, 71]. Such studies of influence of temperature and inorganic salts on chemical processes taking place in fly ash- $\text{Ca}(\text{OH})_2$ blend may be considered as investigations of simplified systems showing, to some degree, what could have happened in early ancient binders under influence of different chemical compounds dissolved in mixing water, for example sulphates and chlorides from sea water in the case of maritime concretes.

It is worth emphasizing that among various ancient structures that we can admire to this day, harbour constructions deserve special interest as they are durable and have remained stable for over 2000 years in aggressive seawater environment. The concrete mixture was composed of: volcanic pumice ash and lime (fundamental binding substances), pieces of volcanic tuff, stone aggregate and sea water [56, 72, 73]. Setting and hardening took place in saline environment of seawater.

At present, it is impossible to determine in details the methods of ancient concrete production as well as variations of ancient sea levels and other conditions of hardening. Thus, it is difficult to explain hardening mechanism and mystery of ancient concrete durability in details. Thorough research of ancient submarine concretes has been carried

out by an international interdisciplinary team of specialists (ROMACONS group) [55, 56, 72–75]. They found that reaction between zeolitic ash, lime, and seawater resulted in the formation of calcium–aluminium–silicate–hydrate phases of different crystalline structures: poorly crystalline C–A–S–H phase which is the main cementitious binder [72, 73, 75] and 1.1 nm Al-tobermorite³ [56, 72, 74] or 1.1 nm tobermorite [73, 75]. The presence of phillipsite [72, 74, 75] and chabazite [73] was also found. Phillipsite can be of geological origin (phillipsite aggregate), but its presence also in relict voids implies crystallization in the concrete structure [72, 74]. Strätlingite crystals were occasionally present [74]. Ettringite, hydrated calcium-chloroaluminates and calcium carbonate were also identified in some samples [72–75]. Halite crusts, hydrotalcite and also rarely brucite were found [75]. It should be emphasized in this place that ancient maritime concretes do not have uniform structure; they have diverse components depending on local conditions. Differences in chemical compositions of these materials are presented above; they may be also found in other reports, e.g. [55].

Analysing the results of the contemporary research on the microstructure of ancient concrete makes another questions appear: what was the mechanism of the formation of above mentioned phases having regard to condition of hardening? How is it possible to form some of these phases next to each other? And finally, what binding phases are responsible for making the strength and durability of ancient underwater concretes? These problems were analysed by the ROMACONS group working on issues related to durability of ancient maritime constructions [56, 72–75] and recently also by other authors [59]. Some similarities between modern and ancient binders were also discussed by us during lectures at the conferences, e.g. [76]. In this work, we also attempted to answer the above questions with particular regard to the analogy to physico-chemical processes taking place in modern binding compounds with similar compositions. Moreover, possibilities to use thermal analysis as complementary method for such investigations were discussed.

Firstly, presence of tobermorite or Al-tobermorite in structure of ancient maritime concrete can be puzzling, because these minerals mainly form in specific conditions: in hydrothermal geological processes (product of alteration of calcium carbonate rocks [75]), in alkaline hydrothermal environments [77], also during hydration of Portland cement in autoclave [11]. Both crystalline products, pure tobermorite and Al-tobermorite, are not found in conventional cement concrete which was cured at room temperature

(amorphous or low-crystalline C–S–H are typical products of cement hydration in such conditions) [56, 72, 74]. Crystalline tobermorite is formed in autoclaving products of a mixture composed of calcium source (cement or calcium hydroxide) and silica at a temperature up to about 140 °C [11]. Mostly it is in form of 1.1 nm tobermorite (the most common form that occurs in nature) but at higher temperatures, it goes into xonotlite [11, 77–79]. In the case of alumina source, Al-tobermorite is created, because Al³⁺ can substitute Si⁴⁺ in silicate chain linkages [80]. In the literature, higher temperature of synthesis in autoclave can also be found, e.g. 180 °C/12 h (quartz sand and calcium oxide with addition of halloysite were raw materials) [81], 185 °C/several hours (raw materials: steel slag, lime, quartz and inorganic admixtures) [82]. At temperature about 200 °C and greater, metastable tobermorite can be formed before its conversion to xonotlite [77, 79, 80]. However, Jackson et al. indicate that in some cases tobermorite can also be created at relatively low temperature, i.e. about 80 °C [56] or even 60 °C [73]. Such a synthesis takes place in the case of alkaline activated silica and zeolite (similar composition that occurred in ancient concretes). Such process takes time from several weeks to several months [56]. Some confirmation of the above may be the fact that the structure of C–A–S–H/Al-tobermorite phase from ancient concrete is similar to C–A–S–H synthesized at elevated temperature (80 °C) [59]. Moreover, according to information given in [79], tobermorite can be synthesized even at room temperature during about 30 days. Some premises, basing on investigation of microstructure of ancient concretes, also indicate a possible post-pozzolanic origin of tobermorite and phillipsite. In such a case, the crystallization processes took place over time in low temperature [74].

During the tobermorite synthesis, amorphous C–S–H gel forms firstly, and then it transforms to ordered crystalline form of tobermorite or xonotlite [77, 80, 83]. Houston et al. [80] indicate three main reaction pathways in CaO–SiO₂–Al₂O₃ system in alkaline media and at elevated temperature: creation of amorphous or low-crystalline C–S–H is the first step, after which growing of semi-crystalline tobermorite takes place, and then recrystallization in solid mass. Reaction rate increases with raising temperature and with content of aluminium which accelerates the formation of tobermorite [77, 79, 83] and retards its recrystallization to xonotlite [79, 83] while alkalis make it easier to obtain tobermorite from zeolite and Ca(OH)₂ [77]. Small amount of some foreign ions can also affect kinetics and mechanism of tobermorite crystallization [79, 82]. For example, positive effect may be observed in the case of presence of small amount of sulphate ions which promote tobermorite crystallization but prevent its transformation to xonotlite [79].

In the case of ancient structures, pH of pore solution equalled 12–14 [74] and environment of reactions was

³ Calcium–aluminium–silicate–hydrate of tobermorite structure in which Si⁴⁺ was partially substituted by Al³⁺.

Table 2 Research methods used for testing the degree of SCMs reaction in SCM-cement system by the use of other methods than thermal analysis and calorimetry

Method	Basis of determination	Benefits and disadvantages, other comments	References
Selective dissolution	Chemical dissolution of unhydrated cement, products of hydration and pozzolanic reaction, leaving unreacted SCM as a residue which can be quantified	<ul style="list-style-type: none"> • often used direct method[*], the reaction degree can be calculated • different solvents can be used for different kinds of SCMs, e.g. EDTA with NaOH, HCl, picric acid, other acids, HCl and Na₂CO₃ • an optimization of sample preparation, proper choice of solvent and method of results calculation are necessary • incomplete dissolution of clinker or hydrated phases can be the source of errors (appropriate correction of calculations should be applied in such case) • some components of SCMs can also be dissolved, in such case calculated degree of SCM reaction may be overestimated (correction of computation should be used preceded by testing of dissolution of pure SCM) • the superfine grains of SCMs can be lost during filtration and as a result of partial dissolution • problems of reproducibility, especially in the case of research carried out by different laboratories • the method is recommended for hardened cement paste only, not for cement concrete and mortar (possibility of partial dissolution of aggregate) • the precision of the method depends on the amount and kind of SCM (the method should not be used in the case of high dissolution of pure SCM) • relatively low cost, simplicity of the determination and no need for the use of specialized equipment 	[22, 27, 37, 40, 41, 49–51]
Image analysis (BSE and EDS from SEM), SEM point-counting technique	Identification and quantification of phases based to their brightness, combination with chemical mapping (EDS), determination and counting of the phases at each point of grid which is superimposed of the SEM image on hardened paste	<ul style="list-style-type: none"> • direct method - degree of reaction can be measured directly from the amount of unhydrated components - useful technique to evaluate the reaction of SCM and clinker phases • gray levels of some phases can be similar to other phases - image processing filters should be used or combination of BSE with EDS, X-ray signal is helpful to distinguish these phases • destruction of some SCM particles during polishing process as well as difficulties of counting small grains may cause some errors of determination • time consuming method 	[22, 27, 40, 41, 43, 49, 50]
Compressive strength of cement-SCM mortars	Compressive strength of cement mortar containing adequate amount of SCM is compared to compressive strength of reference mortar (without SCM), activity index is calculated	<ul style="list-style-type: none"> • indirect method • coefficient of pozzolanic activity can be calculated • method often used in practice, commonly used for determining pozzolanic activity of fly ash • different factors, not only reactivity of SCM, influence compressive strength of cement mortars (e.g. porosity), it may be the source of an error • it is possible to mistakenly assign increasing strength to pozzolanic properties of unreactive fine-grained material mainly because of: acceleration of cement hydration (nucleation effect) and particle packing effect 	[11, 15, 36, 38, 52]
NMR (²⁹ Si or ²⁷ Al MAS NMR)	Estimation of the amount of silicates and aluminates, identification of SCM content in the system	<ul style="list-style-type: none"> • direct method • in some cases the effects of C-S-H and unreacted SCM overlap • time consuming 	[22, 27]

Table 2 (continued)

XRD	Determination of the amount of crystalline phases, or total amount of amorphous phases in the system	<ul style="list-style-type: none"> • direct method • Rietveld method is very useful for identification of crystalline components • using internal or external standard is necessary to determine total amount of amorphous phases but distinguishing the amorphous components is usually not possible • the main products of hydration and pozzolanic reaction as well as components of SCM are amorphous – the XRD method is not very useful for determination of SCM reaction, • methods based on calibrated XRD profiles of individual phases, including amorphous ones (PONKCS method), can be helpful - calibrated SCMs peak profiles enable, to some limit, determination of these components of sample • composition of blended cement and microstructural changes of precipitated C-(A)-S-H may affect the peaks profiles and hinder quantification analysis • accuracy of the method depends on SCM content • overlapping of some signals can cause incorrect interpretation • in the case of PONKCS method, there are some problems with reproducibility of the results obtained in different laboratories 	[27, 39, 40, 53]
Determination of Si and Al in diluted alkaline solution of fly ash	Calculation of the amount of dissolved glass of the fly ash basing on concentrations of dissolved elements	<ul style="list-style-type: none"> • pH of alkaline solution is the same as in pore solution of cement paste • dissolution of fly ash is estimated by comparison of measured concentration of dissolving Si and Al (as a function of time) with presence of these components in glass phase of the SCM 	[50]
Other methods for determining pozzolanic activity	Chapelle test, Frattini test, saturated lime test	<ul style="list-style-type: none"> • methods based on determination of Ca^{2+} in solution being in contact with cement and SCM or $\text{Ca}(\text{OH})_2$ and SCM, $\text{Ca}(\text{OH})_2$ fixed by SCM is estimated, in the case of Frattini test OH^- concentration is also determined • lime to pozzolan ratio is important factor in these determinations • in the case of mix containing cement, soluble components such as Na^+ and K^+ influence the result • correlation can be found between the amount of portlandite consumed and cumulative heat released or compressive strength of mortar 	[11, 38, 48, 52]

*Direct method—degree of SCM reaction is evaluated based on direct measurement of the amount of unreacted SCM remaining in the system

Indirect method—calculation of degree of reacted SCM based on some other measured quantity [27]

solution of inorganic salts which were an effect of the presence of $\text{Ca}(\text{OH})_2$, sea water and volcanic tuff. Thus, one can affirm that composition of ancient concrete (lime + zeolitic tuff + saline seawater) favoured formation of crystalline tobermorite or Al-tobermorite phases, which were created during a relatively long time at temperature lower than 100 °C and even <85 °C provided by exothermic reaction of lime with water in massive construction of the element (heat accumulation) [72]. An adiabatic model of heat evolution in similar structures shows that temperature inside the element was above 60 °C and could reach even to 95 °C.

Moreover, elevated temperature persisted for 2–3 years [56, 72, 74]. Thus, it provided temperature conditions for crystallizing the low-temperature form of tobermorite which presence can improve the mechanical strength of C–S–H phase both at ambient and at elevated temperatures [78]. In the presence of aluminate ions, Al-tobermorite can be formed. Because the aluminium ion charge is lower than the silicon ion, the substitution of silicon by aluminium is balanced by interlayer Ca^{2+} or sodium or potassium cations [83]. Substitution of Si^{4+} by Al^{3+} in tobermorite results in some changes in structure of the material. In the case of Al-tobermorite

the basal interlayer spacing increases compared to tobermorite [72, 83]. At this point it should be noted that traces of tobermorite-like crystals (product of pozzolanic reaction) were identified not only in maritime constructions but also in some other Roman mortars while C–S–H type phase was the main product of reaction between pozzolan and lime [63, 84].

Another doubt which appears in connection with hydration/hardening mechanism of ancient maritime binder is possibility of precipitation of ettringite [73]. Elevated temperature which is favourable in the case of crystallization of tobermorite and Al-tobermorite can be problematic in the case of ettringite because of its thermal stability. This compound is thermally unstable at temperatures above 120 °C [85, 86]; however, at lower temperature ettringite dehydration and decomposition can also occur depending on process conditions.

Ettringite can be found in nature as component of some rocks in the case of calcium-rich, alkaline environments [87]. It is one of products of Portland cement hydration formed typically at early hydration periods, then transformed into monosulfoaluminate [11, 88]. In general, ettringite can be created in water solution from gypsum, aluminate ions and calcium at room temperature. It can crystallize in different forms (needles, spherical clusters, bars or columns) depending on several factors: composition and concentration of pore solution, pH, mechanism of ettringite formation, presence of foreign ions in the structure, etc. [89]. The place in the concrete structure in which ettringite is formed is also important [89, 90]. For example when it crystallizes in empty spaces in pores, typical needle-shaped crystals are formed [89]. Also, depending on the mix composition and conditions of hardening, ettringite can be formed right after addition of water or in subsequent periods after hardening of the composite (so-called delayed ettringite). Low thermal stability of ettringite can be visible on TG curves as rapid mass loss at about 100 °C [87, 91, 92]. Such rapid endothermic mass loss is visible in Fig. 7 for fly ash-Ca(OH)₂ sample admixed with Na₂SO₄. However, presence of ettringite in the system is rather difficult to determine basing on thermal analysis only, because temperature of ettringite decomposition is similar to temperature of dehydration of C–S–H phase. Thus, these endothermic effects of mass losses overlap.

Returning to the problem of possible ettringite crystallization at elevated temperature, at rising temperature ettringite gradually releases molecules of water. Firstly amorphous metaettringite is created, then, with increasing temperature, further structural changes occur. Finally, it decomposes to monosulfoaluminate and sulphate, however in the case of subsequent decrease in temperature and sufficient amount of water, ettringite can be re-created from metastable monosulfoaluminate [89, 93]. Ultimately, in the case of further

drying, decomposition of monosulfoaluminate occurs and formation of hydrogarnet (C₃AH₆) and anhydrite takes place [93]. It should be emphasized that stability of ettringite depends not only on temperature but also on several other factors such as water vapour, pH of water solution and its composition (concentrations of ions), water to solid ratio as well as duration of action of the agent [85, 86, 89, 94, 95]. Moreover thermal stability of ettringite which precipitated in different conditions can also differ as conditions of synthesis influence structure of ettringite [96]. Thus, various ettringite decomposition temperatures can be found in the literature, e.g. in [86, 96, 97]. In general, one can expect that this mineral is stable up to about 60 °C, then between 70 and 90 °C it can transform to monosulfoaluminate [89]. Christensen et al. [88] reported that creation of ettringite depends on temperature and on the kind and amount of reaction components, for example, depending on composition of sample, they observed formation or absence of ettringite up to 68 °C. Ghorab and Kishar [98] stated that ettringite is stable up to 60 °C in alkaline solution of pH about 11. Hall et al. [99] found that, in the presence of water and gypsum impurity, ettringite decomposes rapidly at about 114 ± 1 °C and monosulfoaluminate and bassanite were formed. Reducing water vapour pressure shifts the temperature of ettringite stability to lower values while high humidity increases thermal stability of ettringite [93]. For example, Baquerizo et al. [93] showed that not significant changes in the structure of synthetic ettringite occur in the case of sample conditioned at 80 °C during 50 days in a sufficiently high humidity environment. Kurdowski [100] stated, based on analysis of literature reports, that ettringite is stable up to at least 100 °C in a water vapour saturated atmosphere, while its thermal stability decreases in the presence of alkali. Guimarães et al. [87] showed that dehydration of synthetic ettringite goes in a few stages and can even be observed up to about 260 °C in the case of heating rate 25 °C min⁻¹. Thus, summarizing the above information, it is possible to separate the common part of the temperature range where ettringite and low-temperature form of tobermorite could co-exist in the first several months after making a concrete mixture with water. However, there are some indications that ettringite may also be formed at later periods of hydration/hardening (delayed ettringite).

Regarding to the dependence of ettringite stability on alkalinity, different pH ranges can be found in the literature [89, 95]. It probably results from the fact that durability of ettringite changes depending on the surrounding environment. On average, pH range in which ettringite is stable amounts from about 10 to about 13 [89, 95]. According to [101] pH = 10.7 was set as the minimum limit for the stability of ettringite. Ettringite becomes less stable with increasing alkalinity (above pH = 13). Clark and Brown [102], for example, studied formation of ettringite and

Fig. 6 Roman Pantheon (a) and Colosseum (b), photos by the author

monosulfoaluminate from tricalcium aluminate and gypsum in two different liquid media (deionized water and solution of NaOH) in temperatures 40–80 °C. They found that ettringite was created in the used temperature range, but the rate of its formation was retarded in the case of reaction in solution of higher alkalinity.

pH value of saturated solution of $\text{Ca}(\text{OH})_2$ is 12–13. Thus, assuming that lime was mainly responsible for alkalinity of pore solution, it provides proper conditions for ettringite stability until the pH drops excessively due to pozzolanic reaction.

Elevated temperature of hardening and high pH favours physical incorporation of SO_4^{2-} into C–S–H phase [89, 90, 100, 103–105]. Simultaneously, raising temperature increases the ettringite solubility [98] and thus sulphate ions present in the solution can be bound to C–S–H phase [105]. Dissolution of ettringite at elevated temperature can cause that, depending on hydration conditions, this product may not be formed [105]. Sulphate ions adsorbed on C–S–H are mobile and, in the case of moisture storage, can be available for reaction in further periods after lowering the temperature [89, 90, 95, 100, 105]. Ettringite formed in the period after the material was hardened can cause expansion, stress and microcracking. Expansive character of ettringite depends

Fig. 7 TG, DTG and DTA of 7-days fly ash– $\text{Ca}(\text{OH})_2$ pastes admixed with Na_2SO_4 and cured at room or elevated temperature (hydration was stopped before the measurements by the use of acetone, the same methods and apparatus were used as in the case of results presented in Fig. 3)

on its morphology, location of formation as well as time. For example, ball-form ettringite when precipitated in large spherical air pores is non-expansive until the pore space is not filled [90]. In such case, ettringite seals the structure and contributes to the increase in composite strength. Relatively high porosity, which was found in some core samples of ancient maritime concretes [55], may be the reason of preventing imposition of internal stresses and cracking of the structure.

Fig. 8 IR spectra of samples which thermal analysis results are depicted in Fig. 7 (7th and 28th day of hydration, FTIR spectrophotometer Genesis II (Mattson) was used, samples were prepared as KBr pellets)

Discussing hydration processes occurring in maritime ancient concrete, influence of seawater in comparison with fresh not salty water should be taken into consideration. Modern concrete designed based on Portland cement undergoes chemical corrosion but the main problem related to concrete durability is corrosion of reinforcement steel in contact with seawater. Occurrence and intensity of this process depends on location of concrete and water level. Alternating wetting and drying is harmful, while exposure conditions are safer for cement concrete permanently submerged

in seawater. This is because the saturation state of the salt is achieved, which limits ion diffusion into and from the concrete structure [12]. In the case of composite stored under seawater, precipitation of products of reaction between dissolved salts and binder components can be valuable when they form sealing layer. In this way concrete durability is increased because of reduction of penetration of chloride ions into the structure. Jackson et al. [73, 74] found that calcium chloro-aluminates, similarly as ettringite, were created in ancient maritime concrete in discrete microstructures and voids. Moreover, contrary to contemporary cement concrete, ancient maritime concrete did not contain reinforced steel; thus, the problem of reinforcing steel corrosion does not apply to it.

Summarizing, C–A–S–H, Al-tobermorite as well as zeolite crystallization are probably responsible for high durability of ancient seawater concretes [72, 74]. The place of precipitation of chloride and sulphate salts can also contribute to the durability of concrete [74]. Syntheses of aluminosilicate minerals, mentioned above, in ancient structures have relevance to progress in technology of new high-performance concretes which can be more ecologically friendly compared to Portland cement ones [72]. Ancient marine concrete can be considered prototype of the contemporary one which are designed with the use of SCMs [74].

Despite some sceptical comments on the revelations concerning higher durability of ancient seawater concrete compared to Portland cement concrete [106], it cannot be denied that some similarities between ancient and modern binders can be perceived and detailed discussions about mechanism of their durability development are needed. At present, a lot of construction structures are formed with the use of binders containing aluminosilicate SCMs including pozzolanic fly ash of artificial origin. Taking into account necessity to reduce adverse influence of cement production on natural environment, there is a tendency to reduce the amount of Portland clinker and usage of larger amounts of SCMs in concrete. Such mixtures may need chemical activation; thus, in such case, hydration and pozzolanic reactions go in the presence of solution of additional chemical compounds guaranteeing high pH. Thus, the question should appear in this place: can ancient structures be an inspiration for modern engineers to design long-time durable concrete constructions of assumed composition? Attempting answer the question, discussion about hydration processes in the presence of selected SCMs was made in this paper and especially in its Part II.

C–S–H and C–A–S–H phases formed in the presence of aluminosilicate SCMs

C–S–H is the main product of Portland cement hydration (more specifically hydration of alite (C_3S) and belite (C_2S)). It has layered structure [24, 107] in which interlayer spacing contains calcium and water molecules [107].

C–S–H, when formed at room temperature, has low degree of crystallinity and highly disordered structure; thus X-ray diffraction in the most cases cannot be used for its investigation. Techniques such as TG, DTG, DTA/DSC or IR, NMR spectroscopy are more valuable to elucidate microstructure of this phase. Thermal analysis can be useful to determine the amount of water bound in C–S–H (in the case of synthetic C–S–H—it is possible to estimate its stoichiometric formula), the amount of $Ca(OH)_2$ and $CaCO_3$ [108]. It is worth to mention that C–S–H formed in cement paste is difficult to study because the system is composed of different phases and thus it is very complex and has multifarious texture. Moreover, composition and microstructure of C–S–H are changeable depending on: the kind of cement and its composition, hydration time and degree of hydration, water-to-cement ratio, presence of admixtures (chemical or mineral) and additives, temperature and pressure [24]. Over 30 stable phases can be distinguished in the C–S–H system [77]. It is possible to synthesize C–S–H phases of given C/S ratios, e.g. by mixing adequate amounts of CaO with micro- SiO_2 and deionized water [108]. A large amount of hydrated calcium silicates is a consequence of the ability of calcium atoms to create a coordination polyhedron [CaO_6] with dimensions enabling the coordination of silicon tetrahedral [83]. Presence of SCMs complicates the binding mixture more and influences C–S–H chemistry and microstructure, and, consequently, affects mechanical properties and durability of hardened material. Depending on chemical and physical properties of the material as well as conditions of hardening, several components of hardened cement-SCMs blend can be expected: grains of unhydrated SCMs, C–(A)–S–H⁴ phase (the main product of hydration and pozzolanic reaction), ettringite, carboaluminate phases (which formation is favoured by alumina-rich SCMs) and, in some cases, hydrotalcite-like phases [109]. If $Ca(OH)_2$ is not completely consumed, it is also present in the system similarly as $CaCO_3$ which can be introduced into the mixture with its components or can be formed during carbonation with CO_2 from air.

Depending on binder composition as well as conditions and time of hardening, C–S–H contains different proportions

of the main constituents and also various content of water. In general, in the case of C/S ratio above 1.5, C–S–H can be described as jennite-like type, while in case of lower C/S—tobermorite-like structure [22, 24, 83]. Different other nomenclatures of C–S–H basing on solution equilibrium data or C–S–H structure were also proposed [83, 110]. In tobermorite-like C–S–H gel of low C/S ratio, long silica chains form the microstructure, whereas in the case of high C/S—silica dimmers prevail [107]. C–S–H can precipitate as outer (fibrillar, low density, low-stiffness) and inner (compact homogenous morphology, high density, high-stiffness) product [24, 108, 111]. These kinds of C–S–H differ in C/S ratios and elastic modulus [108] which are closely related to the structure of the material. For example, raising C/S ratio results in reduction of polymerization degree of silicon chain [108, 112], which influences mechanical properties. One may expect that higher polymerization degree results in high elastic modulus; however, the content of water and porosity of the structure are also essential [108]. For example, Alizadeh et al. [113] described, basing also on the reports of other authors, that modulus of elasticity is significantly reduced when interlayer water is removed. C–S–H mechanical properties strictly depend on interlayer distance and compactness. In the case of crystalline C–S–H in form of tobermorite, an increase in the modulus takes place as a result of increase in the mean silicate chain length [113]. Qomi et al. [107] indicated the relation between the high calcium content in interlayers and the increase in elastic modulus for 1.1 nm tobermorite. Hu et al. [111] showed that elastic properties of C–S–H evolve with the hydration degree/time which influence porosity and composition of the structure. This observation related mainly to outer loose-packed product.

As aluminium containing phases (C_3A , C_4AF) are components of Portland cement, one may expect that, despite the fact that C–S–H is the main hydration product, it precipitates not as pure phase but partially Al-substituted. This is because aluminium can replace silicon in the structure of C–S–H [114, 115]. The incorporation of aluminium into C–S–H phase is a fast process as it was shown in kinetic study by Paradal and al. [114]. They concluded that the tobermorite-like structure which was characteristic for synthesized C–S–H phase was also maintained in the case of its Al-substitution form, i.e. C–A–S–H. This phase, when it is synthesized at room temperature, does not show long-range crystallinity; however, its atomistic structure is similar to that of tobermorite [116]. Elevated temperature promotes long-range order. Recently Li et al. [117] published research results concerning atomic environment of Ca, Si, and Al in structure of C–(A)–S–H and morphology of this phase depending on C/S and A/S ratio and equilibration temperatures.

⁴ C–(A)–S–H—hydrated calcium silicates containing or not incorporated aluminium.

Average C/S in the C–S–H in plain cement paste is 0.8–2.0 [83] (typically about 1.7 [24, 25, 107]); however, introduction of aluminosilicate SCMs usually results in lowering mean C/S ratio in hydration product [11, 22–26]; thus, structural changes can be expected as C/S ratio influences interlayer distances [118]. Simultaneously, enriching the system in alumina (e.g. in the case of partial cement replacement by aluminosilicate SCMs) causes that poorly crystalline C–A–S–H phase (analogue of Al-tobermorite [72]) is formed. In the case of sufficiently high availability of Al, secondary products such as C_3AH_6 and C_2ASH_8 can precipitate [117]. Similar conclusion was drawn by L'Hôpital et al. [26], who investigated aluminium uptake by C–S–H phase which was synthesized at 20 °C. They found that the products depend on Al concentration: at low amount of Al only C–A–S–H phase was formed while in the case of its higher amount—other products, such as katoite, C_2ASH_8 and even $Al(OH)_3$, can precipitate in addition to C–A–S–H. It indicates some limit of Al uptake in C–S–H.

Depending on C/S ratio, incorporation of Al into C–S–H can occur in various ways. Substitution in tetrahedrally coordinated silica sites happens for low C/S and is favoured in bridging sites of silica chains [25, 26, 107, 117, 119]. Such Al/Si substitution, i.e. in the bridging position, is thermodynamically favoured contrary to the other sites (pairing, ending) [25, 107, 119]. In the case of high C/S, the replacement takes place in octahedrally coordinated sites in interlayer voids (substitution of Ca by Al) [107].

Curing conditions influence degree of Al substituting for Si in C–S–H gel. Chenguang et al. [115], who investigated the effect of temperature regime on this process taking place in Portland cement paste, showed that the relation between degree of substitution, mean chain length and curing temperature is nonlinear. They claimed that constant temperature of 20 °C is beneficial for the Al incorporation [115]. Investigations of another authors [116] show that at higher temperature of curing, processes of crystallization and cross-linking of C–(A)–S–H are promoted. Li et al. [117] concluded that presence of Al in C–A–S–H structure influences Si–O bonds in silicate tetrahedra leading to their contraction. Thus, Al incorporation results in modification of C–S–H structure and its properties.

A few authors showed the increase in layer spacing in the case of incorporation of Al into C–S–H structure [26, 110, 118]. Kapeluszna et al. [118] demonstrated that with the increase in Al content in C–A–S–H phase (synthesized at temperature 20–25 °C), the interlayer distances increase asymptotically up to some limit value which is higher for sample with lower C/S compared to the one with higher C/S. Authors of [118] concluded also that material of higher content of aluminium has increased amount of bound water and lower crystallinity compared to reference C–S–H. Disruption in crystallinity was also confirmed by

other researchers [110]. However, Geng et al. [116] argued that Al incorporation causes an increase in crystallinity and induces cross-linking of C–(A)–S–H product which was synthesized at 80 °C [116]. Another important conclusion, in the light of changes in structure of solid product in the case of SCM introduction into cement binder, is that low amount of calcium in the system promotes C–A–S–H formation. Thus, it is possible that in the case of SCM–cement paste, higher amount of C–A–S–H phase may be created not only as an effect of higher aluminium content but also as a result of decrease in Ca/Si ratio [118].

Li et al. [112] claimed, based on NMR results, that C–A–S–H phase shows higher polymerization degree and stronger bond strength compared to C–S–H. The length of silicate chains depends on relative contents of components in C–(A)–S–H phase, i.e. it rises as A/S increases and C/S reduces [112]. Increasing of the chain length in the case of Al uptake in C–S–H was also postulated by other authors [26].

Although mechanical properties of C–A–S–H phase are related among others to polymerization degree and cross-linking, and influence of Al on these parameters was presented, there is no simple relation between Al content in C–A–S–H product and its strength and durability. Considerations made by Qomi and al. [107] lead to conclusion that the way of Al incorporation is one of key parameters deciding about mechanical features of C–A–S–H gel. The kind of counter-ion (charge-neutralizing, such as Na^+ , Ca^{2+}) is also important. Authors of [107] argue that in the case of Al/Si substitution, increasing Al content leads to reduction of average elastic modulus of calcium silicate layers; thus Al-containing phase has lower stiffness and pure tetrahedral silica chains are stronger than those in which Al partially substitutes Si. However, in the case of substitution of interlayer Ca with Al, “healing” process may take place consisting of diffusion of Al to vacant silica tetrahedral sites and resulting in cross-linkage between silica chains. In effect, aluminosilicate structure of increased integrity and potentially increased durability and strength can be formed [107].

All considerations and conclusions presented above were made basing mainly on the research results of synthesized C–A–S–H phase or theoretical considerations; however, it should be emphasized that introduction of SCMs into cement mixture changes chemistry of hydration and causes that various kinds of C–(A)–S–H phases can be created [109]. This is not only result of higher content of aluminium in the system. In general, in case of aluminosilicate product formed in cement–SCM paste, reaction environment is more complex compared to conditions of formation of particular phases during synthesis process. Thus, C–(A)–S–H phases formed in various binding mixtures can be different not only in C/S, C/(S + A), A/S ratios and bound water but also in

content of sulphur, sodium, etc. If alkalis are present, they likely replace Ca in the structure of C-(A)-S-H and, in the case of adequate alkali concentration, phase described as, e.g. C-N-A-S-H (in the case of Na⁺ incorporation) can be formed [109, 120]. Silanol deprotonation of the phase and substitution of Si⁴⁺ by Al³⁺ result in charge imbalance and necessity of its compensation by positively charged species which can be alkali ions. Thus, an increase in alkali uptake can take place in such systems [120]. Moreover, L'Hôpital et al. [26] ascertained that higher pH, obtained by KOH presence, favours Al uptake into C-S-H phase. They perceived that alkali environment causes destabilization and dissolution of some Al-products, such as stratlingite and aluminium hydroxide. It increases Al content in liquid phase and results in higher Al incorporation into C-S-H. The same authors in their another work [121] investigated uptake of Na⁺ and K⁺ by synthetic C-A-S-H. They concluded that several factors influence the alkali uptake in C-S-H and C-A-S-H, such as C/S ratio (lower C/S results in higher alkali incorporation) and concentration of alkali, while presence of aluminium in the solid structure and time of hydration may not have significant impact. By contrast, Hong and Glasser [122] claimed that presence of aluminium in C-A-S-H increases alkali binding. They also agree that low C/S increases alkali sorption.

L'Hôpital et al. [121] came to a conclusion that in the case of adequate high alkali concentration, incorporation of Na⁺ or K⁺ in C-A-S-H can change structure of the phase in such a way that interlayer distance decreases and the length of silica chain becomes shorter.

Myers et al. [120] investigated microstructure of C-(N-)A-S-H phase obtained by alkali activation of ground granulated blast furnace slag. They found that the C-(N-)A-S-H structure is cross-linked. The properties of this phase such as A/S ratio, extent of cross-linking and mean length of chain decrease slightly with time. In such system, raising incorporation of Al into cross-linked C-(N-)A-S-H may not lead to increase in the degree of polymerization [120].

Li et al. [112] showed that C/S ratio and incorporation of Al into C-S-H change not only structure of this phase but can also influence carbonation resistance. They found that carbonation products (calcite, vaterite) depend on C/S and A/S ratio, while carbonation resistance depends mainly on the amount of calcium (C/S ratio) in C-(A)-S-H phase and increasing of Al content did not change significantly the resistance on CO₂.

At ambient temperature of reaction, i.e. 20–25 °C, formed product of C-(A)-S-H is amorphous or has poor crystallinity. Creation of crystalline silicate and aluminosilicate forms, such as tobermorite and Al-tobermorite, at elevated temperature was discussed in the previous chapter

of this paper. Both, crystalline or disordered phases can be investigated by thermal analysis which can be considered as important complementary method. Thermal analysis of pure tobermorite and Al-tobermorite reveals dehydration processes and changes in the structure taking place during heating, ultimately leading to complete destruction of the mineral and creation a metastable disordered product [123]. TG curves show continuous mass loss up to about 700 °C. Below 100 °C evaporation of adsorbed water can take place. Then, at temperature range up to about 300 °C (sharp mass loss), dehydration of interlayer water and connected with it transformation of 1.1 nm tobermorite to 0.9 nm tobermorite, occur. At 550–750 °C—further dehydroxylation takes place [123]; however, decomposition of calcite (if it is present in the system) occurs also in that temperature range. The mass losses are accompanied by endothermic effects on DSC. Another effect, which is not connected with any mass loss on TG, can be observed on DSC curve: the exothermic peak with an extreme at about 840–850 °C. It shows recrystallization of tobermorite into wollastonite [79, 81, 123]. Guo et al. [123] presented TG/DSC curves both for tobermorite and Al-substituted tobermorite. It can be shown that, in general, the effects observed for both phases are similar; however, the authors noted that the exothermic peak relating to transformation into wollastonite is sharper in the case of Al-containing sample. Higher total mass loss (at TG) for Al-substituted mineral may indicate higher amount of bound water, but it cannot be clearly confirmed as the samples contained also free water [123].

The mass loss during heating, indicated on TG curves, for C-S-H and C-A-S-H, shows similar effects as for tobermorite and Al-tobermorite, presented above. Continuous mass loss with increasing temperature is observed up to about 800 °C. Renaudin et al. [110] described the main mass losses related to differently combined water: sharp mass loss at 120–150 °C and broad one at 350–800 °C. They indicated that small mass loss below 300 °C may be an effect of weakly bonded carbonate anions [110]. Moreover, discussed above high-temperature exothermic transformation of silicates to wollastonite may also be observed in the case of C-S-H phase. Tajuelo Rodriguez et al. [124] investigated the transformations C-S-H → β-wollastonite → α-wollastonite. They found influence of C/S ratio on temperature of the transformations thus on stability of the forms of wollastonite.

Conclusions

Presented above considerations lead to a few main conclusions:

1. It is undeniable that the increasing level of environmental pollution forces to take radical actions to improve this

situation. It is necessary to implement the principles of sustainable development related to effective reduction of greenhouse gas emissions, rational use of raw materials, utilization of industry by-products, and better use of energy. Such activities are introduced in the cement industry to mitigate its negative influence on environment.

2. Using supplementary cementitious materials as partial replacement of cement clinker is beneficial to make cement and cement composite more ecological, including reduction of CO₂ emission.
3. Properties of cement composites containing SCMs depend on chemical and phase composition of binding mix influencing structure of hardened material. It is necessary to disclose SCMs reactivity and mechanisms of chemical and physical processes taking place in SCMs-cement systems over time and in different conditions, including development of structure of C-(A)-S-H phase.
4. Products that are found in ancient concretes are to some degree similar to those that are formed in cement concrete especially this containing SCMs. Thus, ancient durable concrete can be an inspiration for modern engineers to design new high-performance and more ecologically friendly materials. However, it should be remembered that ancient concretes did not contain reinforced steel which corrosion may reduce durability of present-day cement concrete.
5. Studies of the microstructure of hardened materials and mechanism of hydration/pozzolanic reactions give the possibility to understand the mystery related to their durability and mechanical properties.
6. Many factors affect the structure and, consequently, the mechanical properties and durability of the C-A-S-H phase, such as type of counter-ion, the way and place of Al incorporation etc., as well as external factors such as temperature, time.
7. In the case of systems in which SCMs are the main source of Al ions, it should be taken into account that SCM is usually less reactive than cement and the key factor is the grain dissolution rate.
8. Among different research methods used to investigate processes of binders hydration and formed products, those enabling estimation of SCMs degree of reaction are especially valuable. These methods have advantages but also more or less limitations. Thus, there is a need to find new or develop further used so far methods to enable more precise determination of reactivity of SCMs in compound system of cement paste.
9. Calorimetry and thermal analysis methods are very useful to investigate early and subsequent hydration periods and formed products including those identified in

ancient structures. These techniques can also be used in studies of the degree of SCMs reaction.

Summarizing the above, it is necessary to conduct research on hydration processes and the microstructure of multicomponent cement mixes in order to link them with mechanical properties and durability. Development of research methods for testing degree of SCMs reaction in SCM-cement system is also needed. These will allow better recognition of the problem of material durability and proper forecasting of its long-term properties, as well as optimization of composition and hardening conditions. The discussion on these issues is continued in the Part II of the work in which, among others, selected SCMs and their impact on hydration processes are considered.

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