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Bc. Kateřina Vašíčková



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INFLUENCE OF IONS ON THE EFFICIENCY OF SHRINKAGE REDUCING ADMIXTURES IN ALKALI ACTIVATED SYSTEMS

VLIV IONTŮ NA ÚČINNOST PŘÍSAD REDUKUJÍCH SMRŠTĚNÍ V ALKALICKY AKTIVOVANÝCH SYSTÉMECH

MASTER'S THESIS DIPLOMOVÁ PRÁCE

AUTHOR AUTOR PRÁCE Bc. Kateřina Vašíčková

SUPERVISOR VEDOUCÍ PRÁCE

Ing. Lukáš Kalina, Ph.D.

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stanovení povrchového napětí roztoků elektrolytu v přítomnosti vybraných surfaktantů měření účinnosti SRA v alkalicky aktivovaných systémech stanovení vlivu aktivátoru na hydrataci, mechanické vlastnosti a smrštění alkalicky aktivovaných

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Bc. Kateřina Vašíčková student(ka)

_ _ _ _ _ _ _ _ _ _

Ing. Lukáš Kalina, Ph.D. vedoucí práce prof. RNDr. Josef Jančář, CSc. vedoucí ústavu

_ _ _ _ _ _ _ _ _ _ _ _ _ _

prof. Ing. Martin Weiter, Ph.D. děkan

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ABSTRACT

Alkali activated materials, especially when activated with waterglass, are subjected to substantial drying shrinkage that hinders their broader industrial application. The effect of shrinkage reducing admixtures (SRA), based on poly(propylene glycol), on drying shrinkage of alkali activated blast furnace slag (BFS) mortars was studied. The aim of this thesis is to determine the efficiency of SRA as well as the influence of different type of alkali activator with varying silicate modulus on drying shrinkage characteristics. It was observed that the high amount of alkalis positively influenced the effect of SRA. The higher the amount of alkalis, the lower the drying shrinkage was. It also caused more water to be incorporated in the alkali activated structure and prevent it from evaporation. Thus, the weight change of such mortars was the lowest. Reduced effect of SRA on mechanical strength properties was observed in mortars with low amount of alkalis which was connected with delayed hydration resulting in insufficient amount of created C-S-H gel. The presented thesis further discussed and underlines the role of different kinds of alkali ions as well as their amount on the properties of alkali activated BFS systems.

KEYWORDS

alkali activated materials, blast furnace slag, drying shrinkage, shrinkage reducing admixtures

ABSTRAKT

Alkalicky aktivované materiály vykazují značné smrštění vysycháním, zejména pokud jsou aktivovány vodním sklem, což brání jejich širšímu průmyslovému využití. Tato práce zkoumá vliv přísad redukujících smrštění (SRA) na bázi polypropylenglykolu na smrštení vysycháním alkalicky aktivované vysokopecní strusky (VPS). Cílem této práce je určit účinnost SRA vedoucí ke snížení smrštění vysycháním a zjistit vliv různého typu alkalického aktivátoru s měnícím se silikátovým modulem. Bylo pozorováno, že vysoký obsah alkálií pozitivně ovlivnil účinnost SRA. Čím vyšší množství alkálií bylo v systému, tím docházelo k nižšímu smrštění. Tento jev měl za následek začlenění většího množství vody do alkalicky aktivované struktury, čímž bylo zabráněno jejímu vypaření vedoucímu k nižší hmotnostní změně. Naproti tomu negativní vliv SRA na mechanické vlastnosti byl zaregistrován u malt s nízkým obsahem alkálií, což bylo spojeno i s nízkým stupněm hydratace vedoucí k vytvoření nedostatečného množství C-S-H gelu.

KLÍČOVÁ SLOVA

alkalicky aktivované materiály, vysokopecní struska, smrštění vysycháním, přísady redukující smrštění

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DECLARATION

I declare that I have written my master's thesis on the theme of "Influence of ions on the efficiency of shrinkage reducing admixtures in alkali activated systems" independently, under the guidance of the master's thesis supervisor and using the technical literature and other sources of information which are all quoted in the thesis and detailed in the list of literature at the end of the thesis.

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1 INTRODUCTION

High energy consumption and increased emissions along with aging infrastructure have a harmful impact on our environment. Every year the production of concrete exceeds 10^{10} tonnes/year, which is more than all other man-made materials combined. Such a large production results in approximately 5% of worlds's total anthropogenic greenhouse gas emissions. Nowadays, this fact initiates even more the need for developing more environmentally friendly materials, more durable, highly recycled and energy efficient [1].

Alkali activated materials (AAM) have become materials of interest mainly due to their low environmental impact compared to Portland cement and also due to a possibility of using varieties of industrial waste. Using AAM as an alternative binder instead of the ordinary Portland cement (OPC) adds sustainability to concrete by reducing the CO_2 emissions associated with cement production. [2].

Many scientific studies revealed that some kinds of AAM are distinguished by superior durability and lower heat of hydration compared to OPC binder, high resistance to aggressive environments and good performance in high temperatures. Other advantages are better behaviour upon carbonation as well as better behaviour to freeze-thaw cycles. However, these materials are subjected to drying and autogeneous shrinkage, subsequent formation of microcracks and higher formation of salt efflorescences, being the major drawbacks that hinder their broader industrial application [3], [4], [5], [6], [7], [8].

Only a few authors have studied the possible ways of shrinkage reduction. The effect of shrinkage reducing admixtures (SRA) has been investigated in Portland cement systems, in which they were able to decrease capillary stress in pore solution, thus reducing the shrinkage. However, little attention was dedicated to study of an effect of SRA on alkali activated slag (AAS) systems [8].

This work presents the drying shrinkage characterization of AAS mortars with various types and dosages of activators and the effect of selected SRA on drying shrinkage characteristics. The outcomes of this work can give further insight into drying shrinkage behaviour of AAS and help to understand the shrinkage mechanism.

2 GOALS AND OBJECTIVES OF THE THESIS

The main goal of this thesis is to determine the influence of concentration and ions characteristics of different activators on the efficiency of shrinkage reducing admixtures. To achieve the aim of the thesis, it is essential to accomplish the following partial goals:

- Determination of surface tension of electrolyte solution in presence of selected surfactants,
- SRA efficiency measurement in alkali activated systems,
- Determination of activator influence on hydration, mechanical properties and shrinkage of alkali activated systems.

3 THEORETICAL BACKGROUND

3.1 Alkali activated materials

The alkali activated materials (AAM) are inorganic materials formed by the reaction between alumina-silicate materials and alkaline solution resulting in three dimensional polymeric structure consisting of Si-O-Al bonds. Those materials are the results of complex of chemical processes generally called alkali activation. The alkali activation involves dissolution of raw materials and subsequent polycondensation [9], [10].

3.2 Historical background

Studies of alkali activated materials have a long history in the former Soviet Union, China as well as in Western World. The German chemist **Kühl** was the first scientist whose idea of reaction of the alkali with aluminosilicate precursor was patented in 1908 [11], [12].

Another progress in this problematics was made by **Purdon** in 1940 who tested several samples of blast furnace slag with NaOH solution and also with $Ca(OH)_2$ solution and achieved final strength properties comparable to those in Portland cement.

In the former Soviet Union the work of **Glukhovsky** was focused on alkalicarbonate activation of metallurgical slags on account of a need for alternative materials. Another notable person connected to this research area is **Davidovits** who first came up with the name "geopolymer" and who came up with a number of theories that Egyptian pyramids were built using chemistry resembling alkali activation.

Since the 1990s the alkali activation research grows rapidly in order to limit emissions of CO_2 , which are associated with the production of OPC [12].

There are many different names describing essentially the same material, which causes a confusion. The terms alkali activated materials and geopolymers are generally used the most. The term AAM comprehends any binder system formed by the reaction of alkali metal source with a solid silicate powder (calcium silicate or aluminosilicate-rich precursor, such as slag, fly ash or natural pozzolan). The term geopolymer is often considered a subset of AAM where the calcium content is usually very low to enable formation of highly coordinated structure, to be more precise pseudo-zeolitic network structure [12].

However, according to Davidovits the geopolymers are materials whose ²⁷Al NMR spectra exhibit a peak only about 55 ppm and, moreover, aluminium

might be presented only in coordination 4 in the product structure. Those criteria satisfy the AAM of pure metakaolin only [13].

3.3 Blast furnace slag

Theoretically, any material consisting of silica and aluminium can be alkali-activated. Blast furnace slag (BFS), fly ash, metakaolin and their mixtures are used the most as raw material for alkali activation. The following chapter is dedicated to BFS only [10].

Blast furnace slag is a by-product of iron production in blast furnace. The slag forms in the process of iron ore to iron reduction as a nonmetallic liquid. This liquid floats on the top of molten iron and then the molten slag is separated from the liquid metal and cooled. If the molten slag is quenched rapidly with water, the ground granulated blast furnace slag (GGBFS) is created. Due to its chemical composition and highly amorphous nature the products with high mechanical strengths and with relatively low water demand can be formed [14], [17], [18], [19].

3.3.1 Chemistry of blast furnace slag

From chemical composition perspective, the BFS mainly consists of the following oxides: CaO, MgO, Al_2O_3 , SiO₂. The other components of BFS are, for instance manganese, sulfur, iron and titanium. Typical composition is described in table 3.1. Generally, the composition of BFS depends on iron used. Slow-cooled slag is unreactive and has more crystalline structure whereas rapidly-cooled slag is more amorphous but can have crystalline inclusion too, depending on the chemical composition and processing conditions [20], [21].

The slag contains 90-95% vitreous phase. The crystalline phase consists of solid solutions of gehlenite (2CaO.Al₂O₃.SiO₂) and akermanite (2CaO.MgO.2SiO₂). Both those minerals form tetragonal lattices. However, the reactivity in alkali activation depends on component phases and vitreous phase. The crystalline phase has no hydraulic properties [22], [23].

It was confirmed that the parameter called the degree of depolymerization (DP) largely controls reactivity. It is described as follows:

$$DP = \frac{n(\text{CaO}) - 2n(\text{MgO}) - n(\text{Al}_2\text{O}_3) - n(\text{SO}_3)}{n(\text{SiO}_2) - 2n(\text{MgO}) - 0.5n(\text{Al}_2\text{O}_3)}$$
(3.1)

where n is an amount of substance. This ratio usually ranges from 1.3 to 1.5 for GGBFS. Higher values indicate more depolymerized, thus more silicate network [19].

Constituent	Weight Percent
Lime (CaO)	32 - 45
Magnesium (MgO)	5 - 15
Silica (SiO_2)	32 - 42
Alumina (Al_2O_3)	7 - 16
Sulfur (S)	1 - 2
Iron Oxide (Fe_2O_3)	0.1 - 1.5
Manganese Oxide (MnO)	0.2 - 1.0

Tab. 3.1: Typical composition of the blast furnace slag [20]

The ratios of individual oxides have also the effect on hydraulic activity. In general, ratios of CaO/SiO₂ between 0.5 to 2.0 and Al_2O_3/SiO_2 between 0.1 to 0.6 are considered to be suitable for alkali activation [18], [24].

Another significant parameter that has an influence on the strength development and microstructure is fineness. According to work of **Wang et al.** [18] and **Puertas** [25], the optimal fineness ranges from 400 to 500 m²/kg.

3.3.2 Alkali activation of blast furnace slag based systems

Several alkaline activators of alkali-activated cements and concretes have been described, among them alkaline salts, caustic alkalis, silicates, aluminates or aluminosilicates. Usually, NaOH, Na₂CO₃, Na₂O \cdot nSiO₂ (sodium waterglass) and Na₂SO₄ are the most widely available [27].

The composition of water glass is often characterized by silicate modulus which is the molar ratio between SiO_2 and a corresponding alkali component M_2O . The ratio usually ranges from 1.6 to 4.1 [28], [29].

The alkali activation of BFS based systems is a highly heterogeneous process and comprises several steps. Firstly, the glassy precursor particles are dissolved followed by nucleation and growth of initial solid particles. The process is accompanied by diffusion of reactive species through reaction products. The main reaction product is an aluminium-substituted C-A-S-H gel type with disordered tobermoritelike C-S-H structure. Also, the secondary products, such as AFm phase types, are formed. But the chemistry of AFm phase in BFS systems is not yet well-understood. The structure and composition of C-A-S-H is dependent on a nature of used activator [12].

Yet another scientific paper elaborates on the possibility of replacing Ca²⁺ from the C-A-S-H product by Na⁺ from the activator. This leads to formation of C-(N)-A-S-H inner type gel [26].



Fig. 3.1: Crosslinked and non-crosslinked tobermorite units representing the generalised structure of the C-(N)-A-S-H type gel [16]

NaOH-activated BFS consists of more ordered structure in comparison with the silicate-activated BFS. **Puertas et al.** [15] discovered that the structure of silicate-activated BFS is comparable to tobermorite-like phases. **Myers et al.** [16] created a structural model of those phases with a crosslinked and non-crosslinked tobermorite units enabling the calculation of chain length, Al/Si ration and degree of crosslinking. Scheme of this structure is depicted in figure 3.1.

Also, the activator plays a critical role in the heat evolution characteristics. Shi and Day designed three reaction models according to the shape of calorimetric curves [27].

The first model considers no alkali activator. A contact of ground granulated slag particles with water causes Si-O, Al-O and Ca-O bonds to break on their surface due to the polarization effect of OH^- . As the result of dissolution, there are $(H_2SiO_4)^-$, $(H_3SiO_4)^-$, $(H_4SiO_4)^-$ and Ca^{2+} in water. Due to the fact that the energy of Ca-O bond is much weaker than the energy of Si-O and Al-O bonds, the concentration of Ca^{2+} in water is higher than the concentration of Si and Al species. This leads to formation of Si-Al-rich layer on the surface of slag particle. This layer can adsorb some amount of H⁺ from water, thus OH⁻ ions are made. But the amount of OH⁻ is not sufficient to break enough Si-O and Al-O for the formation of hydration products, C-S-H, C-A-H and C-A-S-H. There is only one small peak observed attributed to wetting and dissolution of slag particles (figure 3.2a) [27].

In the second model NaOH activator was used. There is one significant peak in pre-induction period (attributed to wetting and dissolution) and one peak after induction period which reflects a hydration of slag as it can be seen in 3.2b. Because of the high pH of the activator the Si-O and Al-O are broken as well. A thin layer of hydration products precipitates but no $Ca(OH)_2$ (as observed in Portland cement) [27].

The curve in model III presented in figure 3.2c has two peaks in the pre-induction



Fig. 3.2: Heat evolution curves for alkali-activated slag cements [27]

period (the initial and additional peak) and one hydration peak after the induction period. The initial peak is attributed to wetting and dissolution while the additional peak reflects the reaction between Ca^{2+} from slag particles and anions from the activator. NMR analysis also confirmed the formation of C-S-H gel. Typical activator for this model is Na₂SiO₃ or Na₂CO₃ [27].

A combination of activators can affect the total heat evolution and the amount of added admixtures as well. [27], [30].

Fernández-Jiménez and Palomo studied the influence of a series of factors on mechanical strength behaviour. The nature of alkaline activator turned out to be the most important factor on mechanical strength, followed by activator concentration. A curing temperature and specific surface of slag had a little effect on mechanical behaviour. The mix of Na_2SiO_3 and NaOH leads to the highest strength values, followed by Na_2CO_3 solution. The lowest strengths were obtained with NaOH solution [6].

Puertas compared the composition and structure of AAS pastes activated with different alkaline activator. The significant changes in the composition of pore solution of AAS activated with water glass became evident between 3 and 24 h of reaction when the decrease in the Na content and Si content was revealed. On the other hand, in the pastes activated with NaOH the decrease in Na and Si content was progressive in time. Also, the structure and the composition of the calcium silicate hydrate was different with each activator. The calcium silicate hydrate in the pastes activated with water glass had a low structural order with a low Ca/Si ratio. When NaOH was used as an activator the calcium silicate hydrate exhibited higher structural ordering containing more Al in its structure and higher Ca/Si ratio, compared to systems activated with water glass [31].

3.4 Shrinkage

The reduction in volume at constant temperature without external loading is compatible with the concept of shrinkage. The shrinkage is usually classified into drying shrinkage, autogenous shrinkage and carbonation shrinkage. Drying shrinkage results in the reduction of volume due to water loss and is more discussed in subsection 3.4.1. While autogenous shrinkage is based on the volume changes caused by hydration of cement. When the hydration products of cement react with CO_2 in the environment, the carbonation shrinkage occurs [27], [32].

Alkali activated slag mortars and concretes are subject to extensive drying and autogenous shrinkage [33].

3.4.1 Drying shrinkage

The process involving reduction in volume caused by a loss of water is called drying shrinkage whereas chemical shrinkage results from chemical reactions within a cement paste [34].

Hydrated cement paste has a very porous structure with a wide pore size distribution. This structure with solvation layers is subjected to shrinkage during the desorption [32].

According to suggestion of **Powers** in his work called "Thermodynamics of volume and creep", the combined action of surface free energy, disjoining pressure and capillary pressure within the porous cementitious material participate in drying shrinkage [35].

We can esteem the drying cementitious material to be an open thermodynamic system that exchanges water and gas with surrounding environment. We assume a full saturation at any drying state and also that the system comprises a Gibbs free energy. In agreement with Gibbs-Duhem equality the free energy between two isothermal drying states is a function of change in chemical potential and the change in the components quantity within the open system [32].

The chemical potentials of all constituents in the system have to be equal. Hence, the changes of chemical potentials have to be similar, too. This results in equilibrium between water and vapour. We also presume an ideal gas behaviour of air and water vapour and incompressibility for water ($v_{m,w} = const.$). The Kelvin's law is then given by

$$\Delta p = \frac{RT \cdot \ln \frac{p_{v,1}}{p_{v,0}}}{v_{m,w}} \tag{3.2}$$

where Δp is a pressure due to curvature of the interface (capillary pressure), $p_{v,0}$ is avapour pressure over a plane surface, $p_{v,1}$ is a vapour pressure in equilibrium, and $v_{m,w}$ is a molar volume of liquid.

The Kelvin's equation 3.2 defines the energy balance for the liquid in the equilibrium with its vapour. It describes how the liquid pressure varies due to the curvature of the interface [32].

We consider the atmospheric pressure for drying cementitious matter. The ratio of actual water pressure and saturation pressure is relative humidity (RH). Also, it is assumed that the water pressure is equal to the atmospheric pressure. Then the Kelvin's law reads

$$\Delta p = \frac{RT}{v_{m,w}} \cdot \ln\left(RH\right) \tag{3.3}$$

It is the relative humidity that determines the pressure of the liquid phase, more precisely of the pore solution in case of a cementitious system [32].

In the course of drying leading to water evaporation a high energetic solid/vapour interface is created. The system tries to attain a low interfacial energy, so the total difference in free energy is stored by creating interfacial area at the liquid/vapour interface. The total difference responds to the total mass loss (evaporated water) [36].

It is believed that two types of forces are causing shrinkage of cementitious material, capillary forces and disjoining pressure [32].

Capillary forces

The equilibrium between liquid and vapour occurs if a vapour pressure over a liquid (P) is equal to the saturation vapour pressure (P_0) . This means that the number of leaving molecules from a liquid is the same as a number going to the liquid. This corresponds to the system with the relative humidity of 100%. If the relative humidity is lower than 100%, which means that the vapour pressure is below the saturation pressure, the evaporation takes place [34].

The figure 3.3 shows the difference between the vapour pressure over meniscus and over the plane in capillary pores. The hatched parts represent the number of molecules hindering the evaporation. This number is bigger for the surface with meniscus. It means that equilibrium is achieved at vapour pressure lower than the saturation pressure. The difference between pressures is called capillary pressure P_c . This is described by Laplace's equation

$$\Delta P_c = P_{out} - P_{in} = -\frac{2\gamma}{r} \tag{3.4}$$

where P_{out} is a gas pressure above the meniscus, P_{in} is a pressure inside the liquid, γ is an interfacial tension and r is a radius of a curvature [34], [38].



Fig. 3.3: Effect of capillary pressure on surface [37]

A capillary pressure is proportional to the interfacial tension and inversely proportional to radius of the curvature.

Resulting from the Laplace's equation, a water in capillary pores is under depression, more specifically under tensile stress which must be balanced by compressive stress of the surrounding solid [34].

Shi and Krivenko elaborated the importance of the different type of pores and their effects on properties of hardened cement pastes. Capillary pores form the portion of the space originally filled with water in the fresh cement pastes and has not been filled with cement hydration products. On the contrary, gel pores have size of 1.5 to 2.0 nm, which is the size of water molecule and will not allow the flow of water. Capillary pores with medium capillaries (with diameter 50 - 10 nm) cause moderate surface tension which leads to the shrinkage. On the other hand, gel pores with small capillaries (10 - 2.5 nm) generate strong surface tension resulting in shrinkage. The pores with diameter from 50 to 2 nm are called mesopores [27].

Disjoining pressure

The particles of a cement gel have electrical charge which attract polarized water molecules. A movement of the water molecules into and out of the particles has an effect on spacing between the layers causing the volume changes. This in and out motion induces repulsive forces. On the other hand, the attractive Van der Waals forces between solid layers are suppressed. This is represented as the disjoining pressure that keeps the particles at certain distance [34], [39].

3.4.2 Autogenous shrinkage

Autogenous shrinkage is a tendency of the paste to shrink even in sealed systems, also known as self-desiccation. This type of shrinkage leads to autogenous deformation and might induce early age cracking [40]. Autogenous shrinkage appears as a result of chemical shrinkage. Due to the fact that the volume of hydration products (cement paste) is smaller than the volume of reactants, the reduction in volume occurs at the beginning of hydration process. In plastic state the paste collapses inward on itself. However, at the solid state the air voids begin to form and the materials can resist the chemical shrinkage deformations [32], [40].

During the time that the paste continues to consume water, the tiny menisci occur in the pores of the paste. The hardened, porous material begin to experience autogenous shrinkage and the surface tension of the pore solution creates large capillary stresses [40].

3.5 Shrinkage Reducing Admixtures

Shrinkage reducing admixtures are compounds consisting of organic surfactants that decrease the surface tension of a pore solution. With regard to capillary model described in previous chapter, the decrease of surface tension would reduce a drying shrinkage [41].

The history of SRA is not particularly long. **Sato et al.** introduced the SRA in 1983. In their work they described the shrinkage reduction due to SRA, taking into consideration the capillary forces approach. However, **Ostrikov et al.** came up with similar results even earlier, in 1965, by replacing solvent prior to drying. Over the past two decades, a significant research has been done in the field of SRA. It has been reported that concretes containing SRA have lower shrinkage and also reduced cracking potential [41].

Bentz et al. used X-ray absorption for the examination of the role of SRA. The results showed lower evaporation from mixtures with SRA. They assumed that a concentrated solution of SRA was created at the surface during initial drying, which reduced water transport within the specimen to the surface [41], [42].

The two main groups of SRA are usually classified - SRA containing one type of non-ionic surfactants or mixtures of non-ionic surfactants. It is believed that the non-ionic nature prevents the products from adsorption onto cement phase [32].

There have been distinguished several types of non-ionic surfactants used in SRA, for instance monoalcohols, glycols, alkylether oxyalkalene glycols and polymeric surfactants [32].

3.5.1 Surface activity

A typical surfactant molecule consists of a non-polar hydrocarbon chain alias hydrophobic "tail" and a polar functional group, so-called hydrophilic "head", as shown in figure 3.4. Therefore, the nature of the surfactant is amphiphilic [32].



Fig. 3.4: Simple model of a spherical micelle association [32]

According to the type of used surfactant, the hydrophilic head can vary from a simple hydroxyl radical of a monoalcohol, through more complicated linear multiple head with branched or crossed tails, to block or graft copolymers. The structure of SRA can be tailored to the system in which it is supposed to perform [32].

As mentioned above, the non-ionic surfactant has the ability to reduce the surface tension in which it is incorporated. Water has relatively high surface tension (around 72.6 mN/m at 20°C) because the molecules of water try to squeeze at the surface to minimize surface area so as to minimize the overall energy. While the aqueous solutions of non-ionic surfactants have a decreased surface tension, it means that they have ability to reduce the surface tension at the water/air interface. The same effect is expected in the cementitious materials and so the SRA are of high interest [32].

The amphiphilic nature allows to surfactant to adsorb at the water/air interface where the hydrophilic head is pointed towards water while the hydrophobic tail is oriented towards the air [32].

Figure 3.5 with the plot of surface tension versus the surfactants bulk concentration shows that if the bulk concentration increases, more surfactant molecules are adsorbed at the interface and the surface tension is decreased. The free energy of the system is then reduced [32].

Figure 3.5 also shows that at certain bulk concentration a sharp breaking point appears and the surface tension remains constant above this point. The concentration at which this change is observable is called Critical micelle concentration (CMC) [32].

It implies that the CMC is also crucial for the decrease of surface tension in cementitious materials. Moreover, it is important to mention that a mixing water chemically bound into hydrates can cause an increase of the bulk concentration of SRA during the hydration process. This means that at certain point the SRA concentration might exceed the CMC. This fact also gives us a limit to shrinkage reduction [32].



Fig. 3.5: Surface tension of aqueous solution of surfactant vs. bulk concentration of surfactant [32]

3.5.2 Association and self-aggregation

At low bulk concentration the surfactant molecules exist as single molecules. However, once above the CMC they start to assemble into micelles. The simplest micelle has a spherical shape where the hydrophilic heads form the outer shell and the hydrophobic tails assemble into the core of micelle [32].

The process of micellation is mainly entropy-driven. This entropy increase is explained in two ways [43], [44]:

- Water entropy gain when the micelle is formed the hydrophobic tails assemble into the oil like cores and release water which was previously surrounded around the hydrophobic segments; these water molecules gain a freedom of motion causing the increase of entropy.
- Surfactant entropy gain the hydrophobic chains are supposed to increase their freedom in the non-polar core of the micelle. The entropy gain in this case is thus due to fewer restrictions for orientations and bending of the organic chains.

The higher the surfactant concentration, the more micelles are formed. The repulsive interaction between spherical micelles is indicated. Those repulsions can be diminished by changing the size and shape of micelles. The micelles might then form different types of mesophases, for instance cub phase, hexagonal or lamellar phase [43], [44], [45].

In case of high concentration of surfactant or low concentration of water in a surfactant, water rich and a surfactant rich phase separate and the reverse micelle is formed. The hydrophilic heads are then pointed towards the core and the hydropho-



Fig. 3.6: Simple model of a spherical micelle association [46]

bic tails form the outer shell [32].

The separation of two phases into liquid layer occurs above a certain temperature ("cloud point") which causes the micellar solution to become turbid and cloudy. This temperature is called Lower critical temperature (LCT), the phenomenon is happening due to the differences in density [32].

Tadros explained in his study that liquid crystals or mesophases are formed at the low temperature, increasing bulk concentrations due to entropy contributions. Higher temperature causes stronger repulsions and the hydrophilic are less hydrophilic. This can even lead to turning micellar solution into solution of monomers. Then, the high surfactant concentration causes the phase separation as mentioned above due to an entropy gain. Also, the LCT depends on the molecular architecture of the surfactant, i.e. the ration between length of hydrophobic tail and hydrophilic head group [43], [32].

It can be predicted that the change of temperature (e.g. drying) might result in phase transitions that influence the behaviour of cementitious systems [32].

Salting-in and salting-out effects

In case of non-ionic surfactant in electrolyte solution the self-aggregation is observed. There are two effects that have to be taken into account. The "salting-in" effect initiate solubilisation or miscibility of the surfactant in aqueous electrolyte solution. On the other hand, the "salting-out" effect, which causes the decrease of CMC, lowers the tendencies to phase separation. Due to this effect, the liquid-liquid miscibility gap increases and the self-organisation is enhanced [32].

The effects described above are connected to Hofmeister series or lyotropic series. The ions that promote the salting-out are called cosmotropic or water-structure makers (left of Cl^-). They decrease the solubility of protein in water while the ions right of Cl^- have an ability to increase the solubility of a protein in water. These ions are called chaotropic or water structure breakers [32], [47].

The Hofmeister series thus reads

$$SO_4^{2^-} > HPO_4^{2^-} > OH^- > F^- > HCOO^- > CH_3COO^- > CI^- > Br^- > NO_3^- > I^- > SCN^- > CIO_4^-$$

salting-out salting-in

Fig. 3.7: Hofmeister series [32]

The molecules of water are hydrogen bonded to the hydrophilic moieties of nonionic surfactant. The second layer of water that surrounds the hydrophilic moieties is considered to be a bulk water. The properties of the hydration water are influenced by the presence of salts [32].

It was suggested that a weak cation binding results in a slight cationic character of the non-ionic surfactant micelles, which promotes the salting in effect. This was observed for H⁺, Li⁺, Ag⁺ and also for di- and trivalent cations, such as Ca²⁺ and Al³⁺. Those cations are released by the clinker phase. This would signify that salting-in might exist in the cementititous materials [48].

However, from the work of **Bowron and Finney** it is concluded that in case of cementitious materials the non-ionic surfactants are subjected to salting-out. The experiment shows direct anion-bridging between anion and the hydroxyl groups of two alcohol molecules while the cation remained in its normal hydration shell. The anion-bridging brings about the reorganization where the hydrophobic parts were exposed to the bulk water. They concluded that the whole process is driven by polar interactions and the reorganization was meditated by a ion (in their case by chloride ion). It was suggested that the described polar interactions between hydroxyl groups might promote phase separation[49],[50].

The question is whether the salting-in or salting-out effect dominates in the cementitious system [32].

The paper by **Rosen** [44] described the influence of ions on the CMC of nonionic surfactants follow the Hofmeister anion series. Furthermore, the classification of cation series was found as it is shown in figure 3.8. The salting-in effect dominates on the right of K^+ .

$$NH_4^+ > K^+ > Na^+ > Li^+ > 1/2 Ca^{2+}$$

Fig. 3.8: Cation lyotropic classification [44]

To sum it up, it is assumed that the electrolyte nature of pore solution enhances the salting-out of non-ionic surfactants. This might influence the shrinkage reduction achievable with SRA [32].

3.6 Shrinkage of alkali activated systems

Using alkali activated materials instead of ordinary Portland cement helps to create more sustainable system by reducing CO_2 emissions. However, AAM are connected with a volumetric instability that leads to high shrinkage deformations, which has impeded the acceptance of those materials raised concerns [51], [52].

The researchers from the Pennsylvania State University, **Hailong Ye et al.** [52], focused in their work on the shrinkage of alkali activated slag cements. The drying shrinkage of four different AAS mortars and one control OPC mortar was measured under two types of drying conditions, rapid drying and step-wise drying.

The rapid drying means that the shrinkage is measured at constant relative humidity until the equilibrium is reached, while the step-wise drying involves measuring shrinkage across a broad range of RH. In case of rapid drying, four different relative humidities were used (30, 50, 70 and 85% RHs) whereas in step-wise drying a gradual change of RH from 85 to 30% was applied.

The experimental results gave several conclusions. For rapid drying it was observed that lower RH promotes higher moisture loss and moreover, moisture loss of each AAS mixture is larger than for OPC. Step-wise drying involved drying to equilibrium, and then gradually dropping the RH. The step-wise drying showed higher values of shrinkage than those measured in case of rapid drying. For instance, one particular mixture of AAS where NaOH was used as an activator when dried gradually to RH of 50% showed 77% higher shrinkage deformations than when dried rapidly to the same RH. This indicates that drying shrinkage behavior of AAS materials is highly dependent on the rate of drying.

Hailong Ye et al. also claimed that a creep deformation might contribute to drying shrinkage of AAS. The results showed that the mass loss of AAS mixtures is much faster than that of shrinkage. This means that the mixtures continue to shrink, although they are not losing any more water. This might lead to significant creep deformation in AAS while in case of OPC the shrinkage basically terminates when moisture loss reaches the equilibrium. This is a key information proving that creep plays an important role in drying shrinkage of AAS [52].

The research of **Palacios and Puertas** [33] dealt with the effect of shrinkage reducing admixtures based on poly(propylene glycol) (PPG) on the stability of slag mortars. The sodium waterglass was used as an alkali-activator. SRA was added at dosages 1% and 2%. Also, a cement type CEM I 42.5R was used as a reference material. For the shrinkage measurement the specimens were placed in a humidity chamber at 99% and 50% RH.

The samples cured at RH = 99% with addition of 1% had the flexural strength 25% higher than the mortars without admixture. The flexural strength of AAS

mortars containing 2% of SRA was increased in samples cured under both conditions - 99% and 50% RH, by 75% after 7 days and by more than 100% after 28 days for the samples cured at 99%.



Fig. 3.9: Shrinkage in waterglass-activated slag mortars under different curing conditions: a) RH = 99% and b) RH = 50% [33]

Regarding the shrinkage for the mortars cured at 99% RH with the addition of 1% of SRA reduced the shrinkage by up to 50%, while the addition of 2% diminished shrinkage by up to 85%, having the values similar for Portland cement mortars. The addition of 1% of SRA lowered shrinkage by only 7% and the addition of 2% of SRA reduced shrinkage by up to 50% when cured at 50% RH. Still, in this case the shrinkage was twice as large as in Portland cement mortar. The results are represented in figure 3.9.

It was concluded that SRA had several beneficial effects which included the decrease in the surface tension of the water in the porous system and smaller internal stress when the water evaporated. The redistribution of the porous structure was also observed meaning that SRA increased the percentage of pores with diameter ranging from 0.1 to 1.0 μ m. This resulted in the capillary stress being much lower than without admixture [33].

4 MATERIALS AND METHODS

This chapter elaborates on the used materials as well as on the preparation of samples. It also outlines different samples testing and measurement methods. Some results are already presented here, where no longer discussion is needed.

4.1 Materials

4.1.1 Blast furnace slag

Blast furnace slag was obtained from ArcelorMittal Ostrava, Inc., Czech Republic, having a specific surface of 400 m²/kg. The chemical composition specified by the X-ray fluorescence spectroscopy (XRF) is shown in table 4.1. The crystalline composition of BFS determined by X-ray diffraction (XRD) confirmed the presence of merwinite, melilite, $\beta - C_2S$ and calcite.

Tab. 4.1: Element analysis of pore solution, pastes activated with sodium waterglass

Chemical composition of BFS in wt. $\%$									
SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	SO_3	$\mathrm{Fe}_2\mathrm{O}_3$	${\rm TiO}_2$	MnO
34.7	9.1	41.1	0.4	0.9	10.5	1.4	0.3	1.0	0.6

4.1.2 Alkaline activators

- Liquid sodium waterglass
 - produced by Vodní sklo, a.s.
 - silicate modulus 1.92
 - Na₂O content: 16.15%
 - SiO₂ content: 30.7%
- Liquid potassium waterglass
 - produced by Vodní sklo, a.s.
 - silicate modulus 3.79
 - K₂O content: 8.68%
 - SiO₂ content: 20.98%
- Sodium hydroxide
- Potassium hydroxide

4.1.3 Shrinkage reducing admixture

The poly(propylene glycol) by Sigma Aldrich with the average molecular weight of $M_n = 425$ was used as a shrinkage reducing admixture for all measurements.

4.1.4 Aggregates

Standard sand according to ČSN 196-1 was used for the mortar preparation, more precisely fine sand PG I, medium sand PG II and coarse sand PG III.

4.1.5 Water

The demineralized water produced at the Faculty of Chemistry was used for sample preparation.

4.2 Conductometric analysis of waterglass

It is essential to know the precise composition of waterglass, meaning the content of SiO_2 and M_2O (Na₂O or K₂O), in order to propose an optimal dosage of waterglass into a mixture [53].

The conduct of electrical current is realized by the movement of ions presented in electrolyte solution. The contributions of each ion are attributed to the overall conductivity. Most of the ions contribute equally to conductivity of solution except hydroxide and oxonium ions whose conductivity is several times higher due to the presence of hydrogen bonds [54].

When the waterglass solution is titrated with hydrochloric acid, the following reactions can take place:

$$SiO_3^{2-} + H^+ = HSiO_3^-$$
 (4.1)

$$HSiO_3^- + H^+ = H_2SiO_3 \tag{4.2}$$

The determination of the waterglass composition comprises two titrations. If the silicate modulus of waterglass is equal to 2 or higher, only the second reaction 4.2 finds its use. This means that only one break is observed at the titration curve corresponding to amount of $M_2O(V_{HCl})$, as shown in figure 4.1 [53].

For determination of SiO_2 a suitable excess of NaOH must be added to waterglass before the beginning of conductometric titration. Due to the excess of NaOH the reaction 4.1 also appears so the two breaks are observed at the titration curve. This is represented in figure 4.2. The first break corresponds to OH^- and SiO_3^{2-}



Fig. 4.1: Determination of K₂O, exemplary conductometric curve



Fig. 4.2: Determination of SiO_2 , exemplary conductometric curve

 $(V_{1,\text{HCl}})$ while the second one relates to the amount of $\text{HSiO}_3^ (V_{2,\text{HCl}})$. The content of SiO₂ is calculated from the consumption difference [53].

The added volumes of HCl ($V_{\rm HCl}$, $V_{1,\rm HCl}$, $V_{2,\rm HCl}$, in ml) are then calculated from the points of intersection of the corresponding titration curves. According to those volumes, the content of K₂O and SiO₂ are determined using the equations 4.3 and 4.4, respectively, where $m_{\rm s}$ is a mass of the sample in grams, M is a molar mass of the corresponding substance in mol/g and $c_{\rm HCl}$ is a concentration of hydrochloric acid solution in mol/l.

$$m_{\rm K_{2}O}[\%] = \frac{1}{2} \cdot \frac{c_{\rm HCl} \cdot V_{\rm HCl}}{1000} \cdot M_{\rm Na_{2}O} \cdot \frac{100}{m_{\rm s}}$$
(4.3)

$$m_{\rm SiO_2}[\%] = \frac{c_{\rm HCl} \cdot (V_{2,\rm HCl} - V_{1,\rm HCl})}{1000} \cdot M_{\rm SiO_2} \cdot \frac{100}{m_{\rm s}}$$
(4.4)

The content of Na_2O and SiO_2 in sodium waterglass was determined the same way.

4.3 ICP-OES

The slag pastes with different silicate modulus of activator were prepared. The pore solution was extracted after 24 hours using the press BS-3000 (manufactured by BetonSystem company). After 24 hours, the chemical composition of pore solution did not change substantially and this time also indicates the beginning of drying shrinkage measurement (see subsection 4.5.2). The 100 μ l of pore solution was placed into a 100 ml volumetric flask and filled with water. The samples were then analyzed using Inductively coupled plasma optical emission spectrometry (ICP-OES).

ICP-OES provides a multi-element analysis of solution and also the content of each element in solution can be determined. The plasma energy is given to a sample which causes the component elements to excite. The emission rays are released when the excited atoms return to their lower energy position. The corresponding photon wavelengths are measured. The determination of the element type is based on the position of the photon rays while the content of each element depends on the rays intensity [55].

The content of each element is shown in tables 4.2 and 4.3. The obtained concentrations were then used for other sample preparation as described in section 4.4.

Na_2O pore solution - concentration in mg/l									
M_s	Al	Fe	Mn	Si	Ca	K	Mg	Na	
0.78	0.296	0.020	0.000	2.687	0.003	1.281	0.000	97.701	
0.97	0.243	0.019	0.000	1.903	0.001	0.670	0.000	58.481	
1.29	0.157	0.018	0.000	1.314	0.000	0.302	0.000	33.459	
1.92	0.053	0.005	0.000	3.656	0.000	0.000	0.000	14.493	

Tab. 4.2: Element analysis of pore solution, pastes activated with sodium waterglass

Tab. 4.3: Element analysis of pore solution, pastes activated with potassium waterglass

$ m K_2O$ pore solution - concentration in mg/l										
M_s	Al	Fe	Mn	Si	Ca	Κ	Mg	Na		
0.78	0.225	0.018	0.000	2.269	0.123	137.527	0.004	2.481		
0.97	0.201	0.008	0.000	1.851	0.096	106.188	0.002	1.922		
1.29	0.149	0.004	0.000	1.087	0.099	57.189	0.001	1.182		
1.92	0.083	0.002	0.000	0.821	0.051	22.450	0.001	0.545		

4.4 Surface tension testing

According to element analysis of pore solutions given by ICP-OES measurement, the synthetic pore solutions were prepared for both sodium and potassium waterglass of different silicate modulus. Approximately 30 g of each pore solution was weighed out to 7 plastic flasks, one containing a reference sample and to the other flasks PPG with $M_n = 425$ was added having a mass concentration of 0.05, 0.10, 0.25, 0.50, 1.00 and 2.00 wt.% related to mass of BFS whose amount was corresponding to the amount of used activator necessary for alkali activation.

The surface tension of the prepared samples was then measured by tensiometer BPA-800P (KSV Instruments company) using maximum bubble pressure method. The measurement was carried out in standard mode under laboratory temperature (21°C) meaning that with increasing lifetime of bubble, the flow rate of gas decreased.

The dependence of surface tension of pore solution on SRA concentration was obtained, having enabled to select the most suitable SRA concentration for further measurements and analysis.

4.5 Mortar preparation and testing

The alkali-activated slag mortars were prepared with 0.5 wt.% of SRA related to mass of BFS and without SRA for mechanical strength tests and drying shrinkage tests as well as for workability assessment. The slag was activated with water glass with different silicate modulus as shown in table 4.4. The content of SiO^{4-} remained the same, while the amount of alkalis changed with decreasing silicate modulus. The water/slag ratio was 0.5.

Tab. 4.4: Mortars overview with different silicate modulus

Mortars	Silicate modulus				
Slag + Sodium waterglass + NaOH					
Slag + Sodium waterglass + NaOH + 0.5 wt.\% SRA		0.97	1.29	1.92	
Slag + Potassium waterglass + KOH					
Slag + Potassium waterglass + KOH + $0.5~{\rm wt.\%}$ SRA					

4.5.1 Workability assessment of fresh mortars

The workability assessment of fresh mortars was carried out based on the standard ČSN EN 1015-3 [56]. The mould was filled with a fresh mortar and then removed. The flow table spread was measured in two directions (mutually perpendicular), then the table was shaken 15 times and the flow table spread was measured in two directions again.

4.5.2 Drying Shrinkage testing

The mortar specimens with dimensions $25 \times 25 \times 285$ mm were prepared with 0.5 wt.% of SRA related to mass of BFS for drying shrinkage tests according to ASTM C596. The moulds were filled in with metal contacts before the mortar mixture was added. After 24 hours the specimens were removed from moulds and placed into a humidity chamber at approximately 50% RH until the age of 28 days. During this period, the relative length changes were measured almost every workday at the beginning and then usually every three days using the ASTM C490 dilatometer. At the same time a weight loss was monitored by means of laboratory balance.

Length changes of each specimen were evaluated in accordance with the following equation

$$L = \frac{(L_s - L_{et})(L_0 - L_{et})}{G} \cdot 100 \ (\%)$$
(4.5)

where L_0 is a relative value of specimen measured by dilatometer after the removal from mould (after 24 hours), L_{et} a relative value of etalon, L_s is a relative value of specimen, and G is a distance between contacts.

4.5.3 Mechanical Strength testing

The metal moulds were used for mortar specimen preparation. These specimens with dimensions of $40 \times 40 \times 160$ mm served for flexural strength tests while compressive strength tests were performed on the broken parts of specimens after flexural strength tests. These testes were performed at the age of 24 hours, 7 days and 28 days after specimen preparation based on the standard ČSN EN 196-1. The breaker BS-10 (BetonSystem company) was used for flexural strength testing whilst the press BS-300 served for compressive strength tests.

4.6 Isothermal Conduction Calorimetry

The influence of SRA on hydration of AAS was studied through isothermal conduction calorimetry.

Isothermal conduction calorimetry is a method that measures a thermal power (heat rate) as a function of time at constant temperature. As the heat is produced in the sample, the sample temperature changes which gives rise to a heat flow that is measured by the heat flow sensors. The sample is in an ampoule and then inserted into a holder being in contact with a heat flow sensor on a thermostatic heat sink. There is also a reference system in heat conduction calorimeter in which the inert sample is placed. The difference between the output of the sample and the reference is recorded. This can be converted to the thermal power as a function of time and integrated to get the heat [57], [58].

All calorimetric measurements were performed in TAMAir isothermal conduction calorimeter of company TA Instruments at the temperature of 25°C. For each measurement, 4 g of slag were used and adequate amount of activator. More amount of slag would cause a local overheating. The slag was placed into 15 mL glass flask and the activator was dosed into admixe ampoule. The slag and the activator were inserted into the calorimeter and tempered separately (for approximately 3 hours), then mixed together and stirred for 2 minutes with a teflon stirrer. Using admixe ampoule enables to minimize measurement error to 10%. A siliceous sand was used as a reference sample. The amount of reference was chosen so that it had similar heat capacity as the sample, in this case being 15.5 g of reference.

5 RESULTS AND DISCUSSION

5.1 Surface tension

The goal of surface tension measurement was to find the most suitable SRA concentration for drying shrinkage testing. The dependence of surface tension of pore solutions on SRA concentration is represented in figures 5.1 and 5.2. Each pore solution contained different amount of sodium and potassium activator, respectively.



Fig. 5.1: Surface tension of pore solutions with different silicate moduli of sodium waterglass depending on SRA concentration

In both cases, even small addition of SRA led to a steep drop of surface tension. This effect was also supported with the presence of alkalis. Generally, the more alkalis in the solution presented, the lower the surface tension was, and thus they positively influenced the effect of SRA. This is in agreement with Hofmeister series and salting-in effect [32], [44]. This dependence was observed for all pore solutions. Nevertheless, the surface tension values of pore solutions with $M_s = 0.78$ and 0.97 were basically the same within the deviation values.

It can also be concluded that after a sudden decrease of surface tension the values did not further change sharply but, on the contrary, remained constant more or less for almost all solutions. This phenomenon occurred at the moment when the SRA concentration reached 0.5 wt.%, meaning that the SRA reached its CMC.



Fig. 5.2: Surface tension of pore solutions with different silicate moduli of potassium waterglass depending on SRA concentration

As a consequence, it was concluded that the 0.5 wt.% of SRA should be further added to the samples for the following measurements. It is also worth mentioning that pore solution with sodium ions reached its CMC when the surface tension was between 40 - 50 mJ/m², while for the potassium pore solution this is observed when surface tension is ranging from 45 - 55 mJ/m². This can be explained by the more intensive salting-in effect in case of sodium ions than of potassium ions which is relevant with cation lyotropic series [44].

5.2 Drying shrinkage and weight change

Figure 5.3 represents the drying shrinkage development of mortars activated with waterglass with different silicate modulus with 0.5 wt.% related to the amount of slag and without SRA in the course of 28 days under the curing conditions of 50% RH. The pictures of each mortar specimen after the drying are shown in appendix I.

The lowest drying shrinkage exhibited mortar with $M_s = 1.92$ being reduced by more than 45% when compared to the mortar with $M_s = 1.29$ whose shrinkage was the highest. The dependence that with decreasing amount of alkalis the drying shrinkage increases, is evident for silicate moduli $M_s = 0.78, 0.97$ and 1.29. However, this trend was not observed in case of $M_s = 1.92$ due to delayed and suppressed hydration resulting in small amount of C-S-H gel and changes in pore size distribution (the hydration characteristics are detailed presented in section 5.5). The less mesopores in mortar structure, the lower the capillary pressure is created which means the lower shrinkage. These mesopores would generate a capillary pressure which causes a tension leading to cracking [27]. Also, the amount of alkalis had a positive influence on drying shrinkage. The mortar with the highest amount of alkalis added ($M_s = 0.78$) had similar shrinkage characteristics until 10th day. After that the shrinkage increased but was still the lowest compared to mortars with $M_s = 0.97$ and 1.29.

Comparing the samples with SRA and the reference samples, the efficiency of SRA is evident. The SRA was able to reduce the shrinkage up to 50% and 44% in mortars with $M_s = 1.92$ and 0.97, respectively. The effect was not that strong in mortars with $M_s = 0.97$ and 0.78 where the shrinkage was reduced about 27% and 20%, respectively, but the effect was balanced with the presence of alkalis.



Fig. 5.3: Effect of SRA on drying shrinkage development of samples activated with sodium waterglass



Fig. 5.4: Effect of SRA on weight change development of samples activated with sodium waterglass

The weight changes of mortars activated with sodium waterglass of different silicate modulus in the course of drying are shown in figure 5.4. The most significant weight change was observed for mortar with $M_s = 1.92$ where less amount of created C-S-H gel caused that little water was bound within the structure meaning that more free water was evaporated during drying. The weigh changes of mortars with $M_s = 0.78$, 0.97 and 1.29 are also in agreement with drying shrinkage results. The mortar with $M_s = 1.29$ exhibited the highest shrinkage compared to mortars with $M_s = 0.78$, 0.97, thus the weigh change was significantly higher due to lower amount of incorporated water in the alkali activated structure (and more free water that evaporated) than in case of $M_s = 0.78$, 0.97 where more water was incorporated. The weight change of reference mortars was slightly lower in mortars with $M_s = 1.92$ and $M_s = 1.29$ and remained at the similar value in mortars with $M_s = 0.97$ and $M_s = 0.78$. The weight change of all mortars remained more or less constant after 6 days of curing.

The drying shrinkage of mortars activated with potassium waterglass with dif-



Fig. 5.5: Effect of SRA on drying shrinkage development of samples activated with potassium waterglass

ferent silicate modulus also took place under curing conditions of 50% RH which is represented in figure 5.5. These measurements were carried out only for mortars with SRA since its effect on drying shrinkage has been significantly proven in sodium activated mortars. The lowest shrinkage exhibited the mortars with $M_s = 0.78$ which was about 55% lower than the highest shrinkage of mortars with $M_s = 1.92$ after 28 days of curing. This occurrence is in agreement with the fact that the shrinkage decreased with decreasing silicate modulus. This confirmed that the alkalis enhanced the effect of SRA.

Figure 5.6 depicts the weight change development in the course of drying. Although, the drying shrinkage of mortars with $M_s = 0.97$ was about 36% higher than the shrinkage of mortars with $M_s = 0.78$, both weight changes followed the same development in all stages of curing. The most water was incorporated in the alkali activated structure. On the contrary, the significant weight change of mortars with $M_s = 1.92$ and $M_s = 1.29$ revealed that there was more free water in the structure which eventually evaporated. It is also evident that the weight of all mortars did not markedly change after 6 days of curing and remained almost constant.

Both sodium and potassium activated mortars exhibited a significant decrease



Fig. 5.6: Effect of SRA on weight change development of samples activated with potassium waterglass

of drying shrinkage with an increase of amount of alkalis added. The only exception was a sodium activated mortar $M_s = 1.92$ which exhibited the lowest shrinkage due to the suppressed hydration and lower amount of C-S-H gel formed. But in general, the efficiency of sodium and potassium ions on drying shrinkage was about the same and after a sudden increase of drying shrinkage in early stage, the shrinkage did not change by more than 10% after 5 days of curing and remained at essentially equal values after 12 days of curing. Also, the weight change development followed similar trend in both cases. The weight altered less for sodium activated mortars (with an exception of mortar with $M_s = 1.92$) about 26% for mortars with $M_s = 0.78$ and about 11 - 16% for mortars with $M_s = 0.97$ and 1.29.

5.3 Workability of fresh mortars

The effect of different silicate modulus on workability was observed by this experiment. It was revealed that the amount of alkalis and the type of ion played the critical role in workability assessment.

Figures 5.7 and 5.8 represent the workability of fresh mortars activated with



Fig. 5.7: Workability of fresh mortars activated with sodium ions



Fig. 5.8: Workability of fresh mortars activated with potassium ions

sodium and potassium ions, respectively. The addition of SRA did not affect the workability, i.e. the obtained results were the same for both mortars, with and without SRA. Comparing the flow table spreads, the mortars activated with potassium waterglass of different silicate modulus show very high workability compared to sodium activated mortars. However, this high workability led to difficult sample preparation and worse manipulation. On the other hand, the workability of sodium activated mortars was more convenient for mechanical strength and drying shrinkage testing. In both cases the more alkalis used, the higher the workability.

5.4 Flexural and compressive strength

The flexural strength development of sodium waterglass and hydroxide activated mortars with and without SRA is shown in figures 5.9 and 5.10, respectively. The addition of SRA significantly modified the flexural strengths of mortars with low amount of alkalis, especially of mortars with $M_s = 1.92$ in all stages of curing and it also modified the flexural strength of mortars with $M_s = 1.29$ at early stage, after 24 hours of curing. However, the added SRA had almost no effect on mortars with high amount of alkalis, such as the mortars with $M_s = 0.78$ and 0.97.



Fig. 5.9: Effect of SRA on flexural strength development of samples activated with sodium waterglass

The compressive strength development shows similar trend as the results from flexural strength testing, which is demonstrated in figures 5.11 and 5.12. After 28 days of curing, the mortars with $M_s = 0.78$, 0.97 and also 1.29 reached very high compressive strengths ranging from 75 to 95 MPa. The addition of SRA had no significant effect in these mortars. The delayed hydration and low amount of developed C-S-H had also an impact on compressive strength of mortar with $M_s = 1.92$ whose strength was significantly lower, about 30 MPa after 28 days of curing without added SRA. The addition of SRA reduced the compressive strength of mortar with $M_s = 1.92$ even more, exceeding no more than 15 MPa after 28 days of curing.



Fig. 5.10: Flexural strength development of samples activated with sodium waterglass without SRA



Fig. 5.11: Effect of SRA on compressive strength development of samples activated with sodium waterglass

The flexural strength development of potassium waterglass activated mortars with and without SRA is shown in figures 5.13 and 5.14, respectively. The flexural strengths of mortars with added SRA reached lower values than mortars without surfactant which is the most significant for the mortar with $M_s = 1.92$ in early stages



Fig. 5.12: Compressive strength development of samples activated with sodium waterglass without SRA



Fig. 5.13: Effect of SRA on flexural strength development of samples activated with potassium waterglass

where the values were about 70% of the reference values. But generally the difference in strength was not more than 20 - 25% after 28 days. The development was variable throughout the time and it can be concluded that the higher amount of alkalis led to higher flexural strength. However, the flexural strengths obtained after 28 hours



Fig. 5.14: Flexural strength development of samples activated with potassium waterglass without SRA

were smaller than those obtained after 7 days in mortars with $M_s = 1.92$, 1.29 and 0.97. To obtain more precise and satisfactory results, more than three specimens of each series must be tested.



Fig. 5.15: Effect of SRA on compressive strength development of samples activated with potassium waterglass



Fig. 5.16: Compressive strength development of samples activated with potassium waterglass without SRA

As for the compressive strengths of mortars activated with potassium waterglass, it was confirmed that the strengths were higher with decreasing silicate modulus, which is the most evident for reference mortars as shown in figure 5.16. The strengths of mortars with added SRA, represented in figure 5.15, were more or less the same in early stages and followed the similar trend as described above.

To compare the efficiency of both activators, sodium and potassium, it can be assumed that using presence of sodium ions resulted in higher compressive and flexural strengths. The flexural strength of sodium activated mortars was about 15% higher than that of potassium activated. The compressive strength of sodium activated mortars reached even about 27% higher values than the potassium activated mortars. This might be explained by the ability of ions to dissolve aluminosilicate source material. The ion with small ionic radius is supposed to dissolve the aluminosilicates more and that more Al and Si are liberated in the presence of NaOH than KOH [59]. An exception was sodium activated mortar with $M_s = 1.92$, where low amount of C-S-H gel and delayed hydration caused very low final flexural and compressive strength compared to the mortar with the same silicate modulus but activated with potassium waterglass. In general, it can be declared that the flexural strengths were rather low, in both sodium and potassium activated mortars. On the other hand, the high amount of alkalis led to a progressive development of compressive strengths.

5.5 Isothermal calorimetry

The heat flow evolution curves were recorded for different slag pastes. Figures 5.17 and 5.18 correspond to slag pastes activated with different amount of sodium waterglass and sodium hydroxide with varying silicate modulus ($M_s = 1.92, 1.29, 0.97,$ 0.78), where figure 5.17 shows the heat flow evolution rates for mixtures with added SRA while figure 5.18 demonstrates the curves without SRA. The amount of SRA was always 0.5 wt.% of slag.

These heat flow evolution curves were also recorded for slag pastes activated with potassium waterglass and potassium hydroxide with varying silicate modulus and with and without SRA as shown in figures 5.19 and 5.20, respectively.

The individual peaks relate to various stage of slag activation process. The first initial peak is associated with particle wetting and slag dissolution and the second additional peak is related to primary C-S-H gel formation, both during the socalled pre-induction period. Then the process was followed by induction period where the precipitation of the reaction products took place and the third peak was recorded.



Fig. 5.17: Effect of SRA on heat evolution rate of slag pastes activated with sodium waterglass

In case of activation with sodium ions, very similar curves were recorded for pastes with SRA as well as without SRA, but with some differences in case of the third peak. The initial peak (occurring within the first 30 minutes) reached almost the same



Fig. 5.18: Heat evolution rate of slag pastes activated with sodium waterglass without SRA

heat flow evolution rate for pastes with silicate modulus $M_s = 1.29, 0.97$ and 0.78. The peak for paste with $M_s = 1.92$, having the lowest amount of alkalis, is rather weak. The additional peak was very intense in case of $M_s = 1.29, 0.97$ and 0.78, the highest for the modulus of 1.29 and basically the same for modulus of 0.97and 0.78. On the other hand, the peak of paste with silicate modulus $M_s = 1.92$ was highly suppressed as represented in figures 5.17 and 5.18 which is in agreement with low flexural and compressive strengths measured after 24 hours (see section 5.4). This might be caused by the low amount of sodium ions which are necessary for slag activation. This theory was affirmed by the presence of third peak which was again suppressed for $M_s = 1.92$, and in addition this peak was also very delayed, beginning to occur at approximately 55th hours since the experiment had started. The small peak corresponds to low amount of hydration products (less amount of C-S-H gel was created) and its delay is related to hydration products occur later. This phenomenon has further influence on drying shrinkage as well as on both flexural and compressive strength as described in sections 5.2 and 5.4. The third peak is the most intense for the paste with the lowest silicate modulus $M_s = 0.78$ (which means the highest amount of alkalis) and this peak started to occur first. The third of paste with $M_s = 0.97$ and 1.29 followed, respectively. The third peak also revealed the differences between the slag paste with and without SRA. The addition of SRA delayed the third peak for $M_s = 1.29$ and especially for $M_s = 1.92$, meaning that the SRA has a retardation effect on the AAS hydration, primarily for mixtures with lower amount of alkalis.

The initial peak of pastes activated with potassium ions reaches the highest rate for silicate modulus $M_s = 0.78$ and then decreases for $M_s = 0.97$, 1.29 and 1.92, respectively. The significant additional peak occurs for the paste having $M_s = 1.29$. This peak is otherwise very similar for other samples. The third peak is characterized by the same trend as the initial peak, meaning that the highest heat flow evolution rate is reached with activator having $M_s = 0.78$, then the rate decreases with lower amount of alkalis. Also, the lower amount of alkalis, the more delayed the peak. Moreover, this peak is wider. However, in case of activation with potassium ions the SRA had no significant effect on hydration curves.

Comparing the general trend of the heat flow evolution curves between the activation with sodium ions and potassium ions, it was observed that the rates were similar in both sodium and potassium activated mortars. The measurements showed higher additional peak in the samples with potassium ions but then the rate fell sharply, achieving a similar rate for the third peak as the activation with sodium ions.



Fig. 5.19: Effect of SRA on heat evolution rate of slag pastes activated with potassium waterglass

The effect of SRA on slag hydration is also visible in figure 5.21 representing the cumulative heat release of sodium activated pastes. The total heat release was



Fig. 5.20: Heat evolution rate of slag pastes activated with potassium waterglass without SRA

comparable to pure pastes as well as for pastes with SRA in case of sodium alkali activation. However, the retardation effect of SRA is evident in paste with $M_s = 1.92$ during the first days of hydration. But after the retardation, the hydration reaction continued and the total heat release reached similar values as in pure slag system. Figure 5.21 also indicates that the total heat released increased with decreasing silicate modulus.

The total heat release of potassium activated pastes is not significantly affected by the presence of SRA as shown in figure 5.22. Although, slightly more heat was released in the presence of SRA. Again, it was confirmed that the lower silicate modulus was, the more total heat was released. No retardation effect of SRA was observed in pastes with low amount of alkalis.



Fig. 5.21: Total heat released during the hydration of mortars activated with sodium waterglass



Fig. 5.22: Total heat released during the hydration of mortars activated with potassium waterglass

6 CONCLUSIONS

In this work, the influence of shrinkage reducing admixture (SRA) based on poly(propylene glycol) on drying shrinkage and mechanical properties of AAS was studied. According to the results from surface tension measurement, the poly(propylene glycol) with the average molecular weight of $M_n = 425$ in amount of 0.5 wt.% of slag was selected as the most suitable SRA. Moreover, the effect of SRA was positively influenced by the presence of alkalis. The more alkalis in the solution, the lower the surface tension was. Also, pore solutions with sodium ions reached its CMC in lower values of surface tension. This phenomenon is attributed to salting-in effect that is more intense for sodium ions [44]. Subsequently, four sodium activated mortars and four potassium activated mortars with varying silicate modulus ($M_s = 1.92$, 1.29, 0.97 and 0.78) were exposed to drying conditions of 50% RH during 28 days of curing.

It was observed that varying amount of alkalis had a great influence on drying shrinkage development and positive effect on SRA, meaning that with increasing amount of alkalis (and so with decreasing silicate modulus), the drying shrinkage decreased. In both mortars series, sodium and potassium activated, the mortar with $M_s = 0.78$ exhibited the lowest drying shrinkage (with one exception), followed by mortars with $M_s = 0.97$ and 1.29. However, this trend was not observed for sodium activated mortar with $M_s = 1.92$ whose the drying shrinkage rate was significantly the lowest (about 45% compared to the mortar with $M_s = 1.29$). Data from isothermal calorimetry revealed that this effect is attributed to delayed and suppressed hydration which resulted in the smaller amount of C-S-H gel being created and changes of pore size distribution. The less mesopores in the structure, the lower capillary pressure was, resulting in lower shrinkage. It also explains the highest weight change due to little water bound within the structure meaning that more free water was evaporated in the course of drying. The potassium activated mortars followed the trend mentioned above, in which the amount of alkalis was sufficient to activate the slag in early stages of hydration. The drying shrinkage of mortar with $M_s = 0.78$ was about 55% lower that the highest shrinkage of mortars with $M_s = 1.92$, after 28 days of curing. The higher amount of alkalis caused more water to be incorporated within in the alkali activated structure and preventing water from evaporation. Thus, the weight change of such mortars ($M_s = 0.78$ and 0.97) was the lowest. In general, the efficiency of sodium and potassium ions were about the same and after a sudden increase of drying shrinkage in early stages, the shrinkage did not change by more than 10% after 5 days of curing and remained at essentially equal values after 12 days of curing.

The SRA had a reduced effect on flexural and compressive strengths of mortars

with low amount of alkalis but did not markedly change the strength with lower silicate modulus. However, it had a negative effect on sodium activated mortar with $M_s = 0.78$ where the compressive strength was more than 10% lower with SRA added than without. The delayed hydration and low amount of C-S-H gel in case of sodium activated mortar with $M_s = 1.92$ affected both flexural and compressive strengths. The insufficient amount of developed C-S-H gel resulted in low mechanical properties. The flexural strength did not exceed 3 MPa and compressive strength reached approximately 30 MPa after 28 days. Comparing the efficiency of both ions, the utilization of sodium waterglass and hydroxide resulted in higher compressive and flexural strengths. The compressive strengths were from 75 to 95 MPa for mortars with $M_s = 0.78$, 0.97 and also 1.29 after 28 days of curing which were about 27% higher than the values of potassium activated mortars. In general, it can be claimed that the flexural strengths did not reach tremendously high values in both sodium and potassium activated mortars, but on the other hand, the high amount of alkalis led to progressive development of compressive strengths.

On the basis of the obtained results, it can be stated that the selected SRA proved to play a critical role on drying shrinkage development. Its efficiency is also highly supported by the amount of alkalis in activator. These pieces of knowledge point out the importance of using AAM and outline the way of improving their properties, which can boost their broader industrial applications.

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8 LIST OF ABBREVIATIONS

Abbreviation	Description
AAM	alkali activated materials
AAS	alkali activated slag
AFm	calcium aluminate monosulfate
ASTM	American Society for Testing
$\beta - C_2 S$	β -dicalcium silicate
BFS	blast furnace slag
$(2CaO.Al_2O_3.SiO_2)$	gehlenite
$(2CaO.MgO.2SiO_2)$	akermanite
C-A-H	calcium aluminium hydrate
C-A-S-H	calcium-aluminosilicate hydrate
C-(N)-A-S-H	calcium-(sodium) aluminosilicate hydrate
C-S-H	calcium silicate hydrate
CMC	Critical micelle concentration
CSN	Czech state standard
EDX	energy-dispersive X-ray spectroscopy
GGBFS	ground granulated blast furnace slag
ICP-OES	inductively coupled plasma optical emission spectrometry
LCT	Lower critical temperature
NMR	nuclear magnetic resonance
OPC	ordinary Portland cement
PPG	poly(propylene glycol)
RH	relative humidity
SEM	scanning electron microscopy
SRA	shrinkage reducing admixture
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy

9 LIST OF SYMBOLS AND PHYSICAL QUAN-TITIES

Symbol	Description	Unit
DP	degree of depolymerization	-
γ	interfacial tension	mJ/m^2 , mN/m
L	relative value given by dilatometer	-
M	molar mass	g/mol
M_n	average molecular weight	g/mol
M_s	silicate modulus	-
n	amount of substance	mol
Δp	capillary pressure	Pa
P_{in}	pressure inside the liquid	Pa
P_{out}	gas pressure above the meniscus	Pa
$p_{v,0}$	vapour pressure over a plane surface	Pa
$p_{v,1}$	vapour pressure in equilibrium	Pa
r	radius over a curvature	m
R	gas constant	$\rm J/K/mol$
Т	thermodynamic temperature	Κ
V	volume	mL
$v_{m,w}$	molar volume of liquid	$\rm m^3/mol$

APPENDICES

I APPENDIX: MORTARS SPECIMENS AFTER DRYING



(a) Sodium activation

(b) Potassium activation

Fig. I.1: Mortars activated with waterglass after 28 days of curing (the mortar with the highest modulus is on the left)



Fig. I.2: Mortars activated with sodium waterglass (the mortar with the highest modulus is on the left)



Fig. I.3: Mortars activated with potassium waterglass (the mortar with the highest modulus is on the left)