Maturation and structure formation processes can lead to crack formation in silicate and aluminosilicate binders (e.g. for coating materials...) through restricted deformation, loss of strength and thus to loss of durability. These processes are evaluated with silicate materials with an outlook on aluminosilicate binders.

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Maturation and Structure Formation Processes in Binders with Aqueous Alkali-Silicate Solutions

1. Introduction

The "petrification" of organic materials primarily takes place in areas with former volcanic activity, thus with glassy rocks and high K_2O and Na_2O contents. After rainfalls, the alkalinity leads to the formation of glass-like and migration-capable solutions, which predominantly consist of monomer silica species. These species initially form amorphous silica networks during petrification/silicification, which become transformed into quartz through opal as a result of maturation processes [1].

Maturation processes also take place at the aggregation of aqueous alkali silicates (water glasses). Thereby a sol-gel transition is initiated in the silica species dissolved in the water glasses through the initiation of aggregation processes. The gel point is defined in this processes as the range in which the solid phase is bounded together to form a macroscopic unit, thus building up rigidity. It describes the state of the silica system where external gelation can be observed. In turn, the characterisation of the gel point strongly depends on the measuring method used. The gel point can be described by measurement of a significant increase of viscosity in the water glasses after addition of an additive or through rigidity research on the silica formulations by using ultrasonic.

After the gel point, the created silica networks compress further through contraction as a result of further water release or bond formation through condensation reactions. These processes are also the result of decreased stabilisation through progressive carbonation of the potassium hydroxide.

Such compression or maturation processes take place after the gel point with restricted deformation under tension building-up. In the case of pronounced compression processes, the built-up stresses exceed the maximum stress capacity of the rigidifying silica system. This results in the formation of cracks, reduction of firmness or pronounced deformations.

In order to understand in more detail the gelation of water glasses with regard to the formation of early-compact silica networks and thus of durable, crack-free and water-resistant materials, the sol-gel transformation of silicate binders is described here; on this basis, conclusions are drawn about tests to guarantee the durability of the aluminosilicate binders (geopolymers). Chapters 1 to 5 include to a large extent parts of the theoretical aspects and results of the dissertation of K. Schuch [2]; conclusions about aluminosilicate binders are drawn on this basis.

2. <u>Electrostatic and structural aspects of aggregation</u>

The colloidal silica species are primarily stabilised by electrostatic forces in the dispersion medium (aqueous electrolyte). This requires the presence of charges on the surfaces of the particles and in the border area to the surface. Negative surface charges are present in the water glasses, compensated for by the alkali counterions (K^+, Na^+, or Li^+).

Thereby the counterions form a diffuse ion layer around the silica particles. The repelling forces of these layers in the intermediate area between two silica particles stabilise the water glass sol. The size of these double layers depends on the type and concentration of the electrolytes, the dielectric properties of the dispersion medium, and on the zeta potential.

If two silica particles approach each other in the water glass sols, e.g. through the addition of gelation initiators, their double layers will overlap. Thereby not just electrostatic repellent forces are at work but also attracting van der Waals forces. A theory was developed in the 1940s by <u>D</u>ERJAGIN and <u>L</u>ANDAU as well as by <u>V</u>ERWEY and <u>O</u>VERBEEK to describe the reaction mechanism caused by such simultaneously acting attracting and repellent forces. This theory is known as the DLVO theory [3]. The resulting potential flow is positive if the repellent energies dominate. The reduction of the positive potential flow after adding gelation initiators leads to an increased probability of silica particle agglomeration. The silica particles can condense or aggregate with one another unimpeded if the energy barrier is removed or if the negative energies dominate. Here, the DLVO theory considers in a purely formal manner the stability and particle diameter of the initial water glasses as this relates to the reduction of the stabilising energy barriers after adding salts or changing the pH value (electrostatic aspects). Neither can direct conclusions be made about the effect of the additives – reactively building themselves into the silica network –, nor can this lead to better understanding of the dissolution kinetics of the solid additives. By implication, however, the experimental findings on gel formation can be interpreted by using the DLVO theory; furthermore, conclusions for questions pertaining to

usage can be deduced. This makes the importance of the DLVO theory for the activation of targeted network formation visible, assessable, and useful.

Besides the electrostatic considerations regarding the stability of silica particles, geometric, structural aspects should also be included in the considerations about the stability of the colloidal species. Fewer counterions are available for stabilisation of the silica species with increasing water glass modulus (molar ratio = n_{SiO2}/n_{K2O}). The number of highly condensed silica species and thus the average molar mass and the oligomer-monomer ratio increase with increasing modulus ratios. The percolation theory can be included to statistically model the gelation behaviour of the alkali-silicate solutions as regards the geometrical aspects [4]. The percolation theory models the network and rigidity formation of gelation through random occupation of a defined grid with points. Depending on the input parameters (geometric aspects: number and size of the silica species), comparable conclusions can be drawn here regarding the gelation velocity, compactness, and hence the density of the silica network at the gel point of various water glasses. In a statistical model such as that of the percolation theory, the gel point is considered as a coherent network of points connecting the edges of a grid with each other. The theoretical results of the percolation theory can confirm the gelation experiments with the initial water glasses as well as the deformation and strength tests on largely solidified silica formulations.

3. <u>Reactions of targeted gelation through addition of gel initiators</u>

All the water glass additives to be introduced below cause a reduction of the stability of the alkali-silicate solution and thus initiate gelation. It cannot be deduced from the formal reaction equations a to g of the material components how much water is still present at the gel point of the silica network. This can lead to further shrinking of the network and thus to the build-up of stresses. No conclusion can be drawn about the silica species in the initial water glasses, the silica network that forms at the gel point, or the gelation velocity.

a)   Effect of CO_2:
$$K_2O \cdot xSiO_2 \cdot yH_2O + CO_2 \longrightarrow xSiO_2 \cdot (y-z)H_2O + K_2CO_3 + zH_2O$$

b)   Reactions with acids:
$$K_2O \cdot xSiO_2 \cdot yH_2O + H_2SO_4 \rightarrow xSiO_2 \cdot (y-z)H_2O + K_2SO_4 + zH_2O$$

c)   Reactions with Carboxylic acid esters:
$$K_2O \cdot xSiO_2 \cdot yH_2O + 2CH_3COOC_2H_5 \rightarrow xSiO_2 \cdot (y-1)H_2O + 2CH_3COOK + 2C_2H_5OH$$

d)   Addition of cyclo-phosphates, Example Sodium Phosphate [5]:

$$2(Na_2O*xSiO_2+yH_2O) + Na_3(PO_3)_3 \rightarrow Na_2O*2xSiO_2*2yH_2O + Na_5P_3O_{10}$$

e)   Gel initiation by neutral salts [2]:

$$K_2O*xSiO_2*yH_2O + CaSO_4 \rightarrow K_2O*xSiO_2*(y-z)H_2O + Ca^{2+}(\tfrac{z}{2}H_2O) + SO_4^{2-}(\tfrac{z}{2}H_2O)$$

f)   Disruption of the equilibrium by the addition of metakaolin:

$$K_2O*xSiO_2*yH_2O + n[Al_2O_3*2SiO_2] \rightarrow K_2O*(x+2n)SiO_2*nAl_2O_3*(y-z)H_2O + zH_2O$$

g)   Disruption of the equilibrium by the addition of silica gel:

$$K_2O*xSiO_2*yH_2O + nSiO_2*mH_2O \rightarrow K_2O*(x+n)SiO_2*(y+m-z)H_2O + zH_2O$$

With the gelations a to d, the pH-value is reduced through the addition of acidic components, whereby the stabilising alkali oxide is removed from the water glass equilibrium, which leads to increasing the molar ratio ($MVZ = n_{SiO2}/n_{K2O}$) by initiating condensation reactions. With gelation e, the electrostatic stability of the water glasses is influenced by the dissolution of neural salt and the release of twice charged ions, so that gelation is initiated. With gelations f and g, the water glass modulus is increased through the addition of autonomously network-forming components, by partially dissolving solid matter additives into the alkaline water glass solution and initiated bond formation through condensation reactions. The equilibrium is shifted towards to the side of the condensation products.

4. <u>Theories on network formation in water glass solution (structure formation)</u>

The structure formation in aqueous silicate solutions can be described using various theoretical approaches. Points of departure are, for example, the presence of H^+ or OH^- ions in the acidic or alkaline pH-range or aggregation kinetics determined through mechanisms.

4.1 Network formation in acidic and alkaline environment

The gelation of monomeric silicic acids under different conditions is illustrated to ILER [6] in Figure 1. Finely branched silica networks develop if the pH-value is reduced below 7 via Path I or if the pH-value is increased above 7 after adding salt. Via Path II, spherical and compact particles only develop in the alkaline range up to pH value 10, to which then further

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monomers or oligomers bind. An increase of SiO_2 particles (with decreasing curvature radius) can be determined in this pH range, which decreases the likeliness of a reaction occurring.

The SiO_2 particles have reached a stable size. The silica particles continue to grow very slowly through the dissolution of smaller particles and precipitation of silicon dioxide on larger particles. With the tendency to achieve a smallest-possible surface-to-volume ratio, this naturally takes place with a large number of Si-O-Si bonds and a small number of Si-OH- groups. From a pH value larger than 10.5, individual monomers and oligomers are released from the solid matter particles of the silica sols. The fast surface size increase combined with the presence of deprotonated SiO_2-particle–O^- causes the zeta potential to significantly rise at pH values higher than 10.5. In this stable range, the water glasses are present with particles sizes of $\leq$ 1.5 nm.
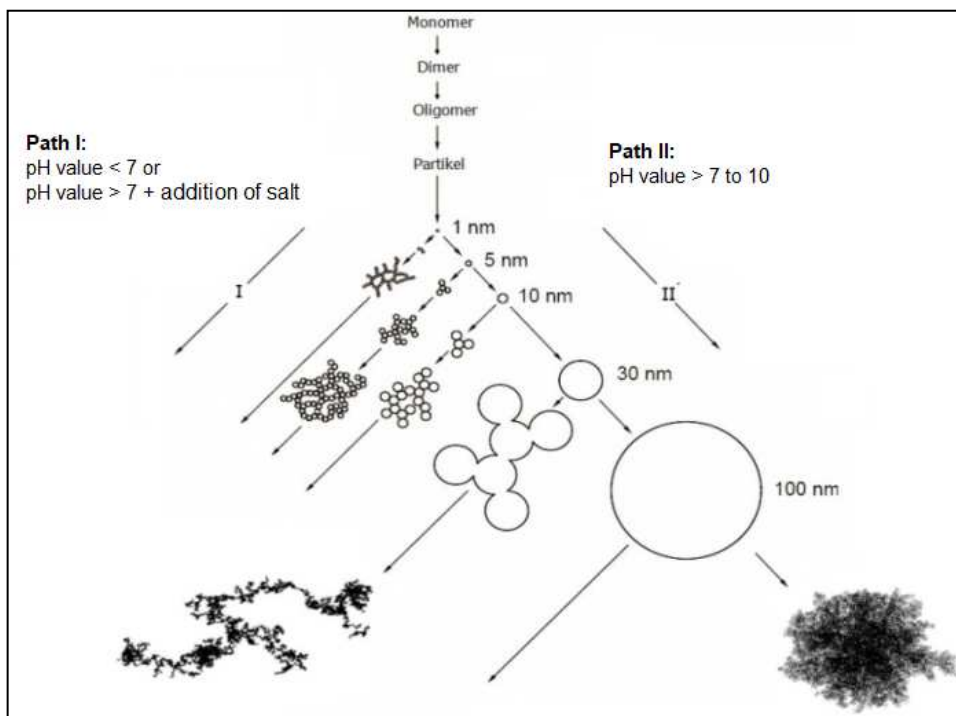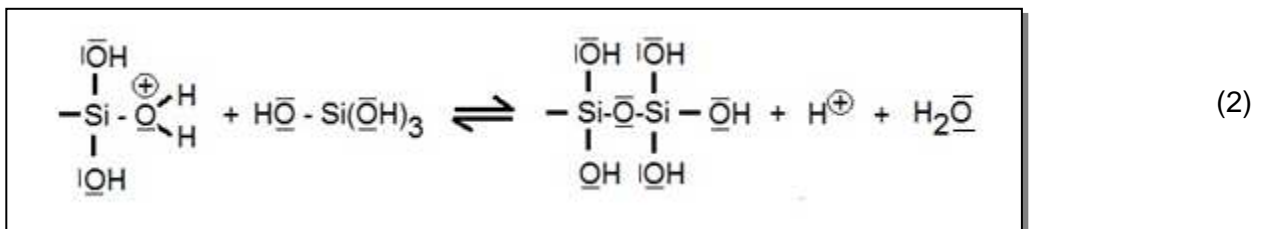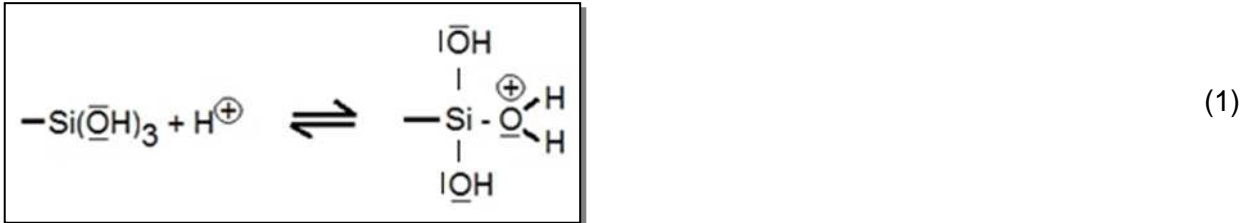

Figure 1: Condensation of the silicic acid

H$^+$-catalysed / OH$^-$-catalysed condensation of the dissolved silica species

The differences between Paths I and II should be explained below to BRINKLER and SCHERER [4]. The electron density at the silicon decreases from Si-OH to Si-O-Si and thus its alkaline nature weakens. In the alkaline environment (Path II), the binder will more likely react to more-condensed or already-connected Si atoms; on the other hand, in the acidic environment (Path I), to the less-condensed silicon atom and thus in the peripheral area.
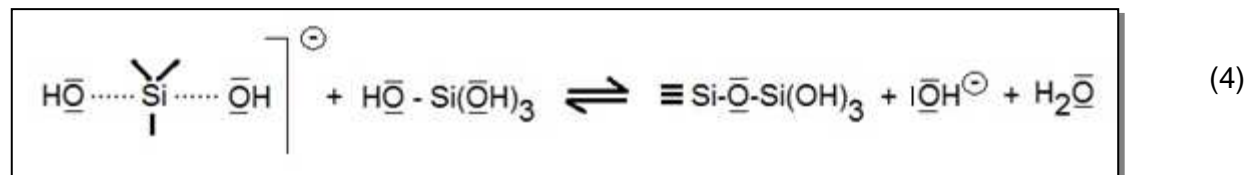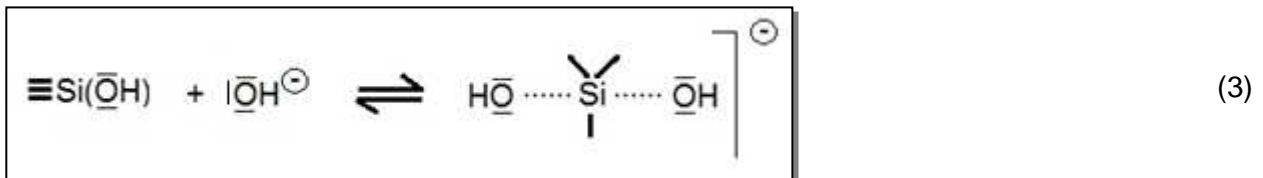
Gelation in the acidic range (examples a to d, chapter 3):

Path I: H⁺-catalysed condensation at less-condensed silicate (greater electron density at the silicon):

$$-Si(\bar{O}H)_3 + H^{\oplus} \rightleftharpoons -Si-\overset{|}{\underset{|}{O}}^{\oplus}\!\!\!\diagdown\!\!{}^{H}_{H}$$

(1)

$$-\overset{I\bar{O}H}{\underset{I\underline{O}H}{Si}}-\underset{H}{\overset{\oplus}{O}}\!\!\!\diagdown\!\!{}^{H}_{H} + H\bar{O}-Si(\bar{O}H)_3 \rightleftharpoons -\overset{I\bar{O}H\ I\bar{O}H}{\underset{\underline{O}H\ I\underline{O}H}{Si-\bar{O}-Si}}-\bar{O}H + H^{\oplus} + H_2\bar{O}$$

(2)

Gelation in the alkaline range (examples e to g, chapter 3):

Path II: OH⁻-catalysed condensation at more-condensed silicate (low electron density at the silicon):

$$\equiv Si(\bar{O}H) + I\bar{O}H^{\ominus} \rightleftharpoons \left[H\bar{O}\cdots\overset{\vee}{\underset{|}{Si}}\cdots\bar{O}H \right]^{\ominus}$$

(3)

$$\left[H\bar{O}\cdots\overset{\vee}{\underset{|}{Si}}\cdots\bar{O}H \right]^{\ominus} + H\bar{O}-Si(\bar{O}H)_3 \rightleftharpoons \equiv Si-\bar{O}-Si(OH)_3 + I\bar{O}H^{\ominus} + H_2\bar{O}$$

(4)

Path I differs from Path II at the location where the silicic acid binds to the existing network. The silicic acid binds to the core of the respective network with Path II, spherically solidifying the network. Deposits form on the peripheral area in acidic environment or by adding acids via Path I. This makes the formed network finely branched.

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4.2 Networks of fast and slow aggregation

The electrostatic stability of the water glasses is reduced by the addition of "neutral" salts which do not significantly change the pH value in water. Which networks are forming thereby, compared to the "acidic" and "alkaline" salts, depends in turn on the solubility of the salt. The silica networks formed by the addition of neutral salts are explained below through the mechanism of slow and fast aggregation. Adding neutral salts changes the resulting potential flow in accordance with the DLVO theory, reducing the stability of the alkali-silicate solution through the reduced energy barrier, whereby the attracting potentials can also predominate. In this case, each collision of silicate ions will lead to a condensation reaction or binding. The binding probability for a collision is one. This is termed a diffusion-controlled or fast aggregation, the so-called diffusion-limited aggregation (DLA). The velocity of this aggregation is primarily determined only by the diffusion process. Silicate particles, which now come into contact with a growing aggregate, are deposited in the case of DLA primarily on the periphery. This leads to loose and enlarged silicate structures, pursuant to Path I in Figure 1. The aggregation behaves differently when there is still an energy barrier present in the resulting potential flow, which has not been fully broken down. This is termed a reaction-limited aggregation (RLA). If an energy barrier E_{max} needs to be overcome, the approaching particles need to make multiple attempts before they condensate. The conditions for this are clearly more pronounced in the inner part of a network with close, frequent contacts to many network sub-structures (collision probability) than at the periphery. This results in significantly more compact and dense structures. The aggregation of aqueous silicate solutions, also called RLA and DLA mechanism, has already been researched by WIJNEN in 1991 [7].

The significant characteristics of a mechanism following an RLA aggregation, compared to a mechanism of a DLA aggregation, are:

- slower gelation velocity
- development of more compact, denser, and tougher silicate networks
- less pronounced post-densification of the silicate network after the sol-gel transformation

5. Deductions for silicate binders

After the gel point, quickly formed aggregations (DLA) enclose a lot of water in the finely branched silicate network. On the one hand, the evaporation of the water should lead to further contractions of the silicate network after gel formation; on the other hand, the finely branched structures, while being exposed to water and progressive carbonation, can reorganise

themselves, which also leads to pronounced compressions. If these compression processes after the gel point take place under restrained deformation, stresses are built up depending on the level of compression in the silicate material, which can exceed the maximum absorbable stresses as a result of increasing rigidity. The quickly occurring aggregation processes further lead to the build-up of high stresses at an early stage of the DLA mechanism, which cannot be absorbed by the emerging finely branched silicate network.

The results of pronounced compression processes and too quickly-forming aggregation are adverse phenomena during silicate coating, which occur in bond and therefore under strain:

- crack formations / late crack formations / loss of strength
- selective or surface exudation as a result of inner contraction of the network
- loss of water resistance / high weathering rates

In order to build up stable, crack-free, and durable silicate materials, knowledge about the emerging silicate network at gelation, the gelation velocity as well as the size and number of silica species in the initial water glasses is therefore of vital importance. Crack formation, late crack formations as well as loss of water resistance are caused by less dense and compact silicate networks after gelation and too quickly occurring aggregation kinetics.

The use of specially selected neutral salt as a gelation initiator and an initial water glass have led to the creation of a compact silicate network during gelation to purely silicate binders, which requires a low level of self-organisation (adverse maturation) and builds up less shrinkage stresses. The development of rigidity of the silicate coating allowed it to absorb persisting shrinkage stress, which prevented the crack formation. Theoretical and experimental investigations of silicate binders led to the following conclusions [2]:

The characterisation of neutral salts on gelation occurred in a silicate binder as a result of stiffness investigations by using ultrasonic and DLVO assessments. The water glasses were evaluated in a comparative approach by using gelation experiments and were interpreted through model calculations by using the percolation theory.

The investigations took place in three potassium water glasses with varying modulus ratios. It was found that the potassium water glass system (SiO_2-K_2O-H_2O) with increasing molar modulus MVZ (n_{SiO2}/n_{K2O}: 1.0; 2.9; 3.9) showed decreasing pH values (pH: 13.0; 11.9; 11.4) and increasing pre-structuring in the form of larger silicate clusters (particle size up to the nm-range). According to the spectroscopic analyses of HUNT et al. [8], an increase of the peak area ratios A_O/A_M (A_O: oligomer; A_M: monomer) for the transition of module 1.0 to 2.9 can be estimated to be by a factor of about 10. Subsequently, the water glass with a modulus ratio of 1.0 can be

classified as low-modulus, the one with ratio of 2.9 as medium-modulus, and the water glass with ratio of 3.9 as high-modulus.

In order to minimise the stresses resulting from the maturation processes caused by compression processes after the gel point, the medium-modulus and high-modulus water glass, which gave a higher oligomer/monomer ratio, are more closely taken into consideration. These two water glasses were more closely investigated with respect to the properties of a RLA or DLA mechanism. For this purpose, the gelation velocities of both water glasses were theoretically analysed by using the percolation theory and experimentally verified through gelation experiments. The model network building was described on the basis of the percolation theory by using the sizes and numbers of the start-silicate clusters of both water glasses ("geometrics" aspects). Thereby it was shown for the medium-modulus water glass that a significantly larger number of necessary percolation steps and denser percolation patterns up to the percolation point (gel point) have taken place compared to the higher-modulus water glasses. Correspondingly, after acid-initiated aggregation (Triacetin), the medium-modulus water glass (MVZ: 2.9) shows lower gelation velocity (n_{SiO2}/n_{Ac} t = 0,18 min^{-1}) compared to the high-modulus water glass (0.40 min^{-1}), whereby the characteristic of an advantageous RLA mechanism is more pronounced compared to high-modulus water glass. It is obvious that the pre-structuring (to large particles) is well-advanced in such high-modulus water glass (MVZ: 3.9), so that the high gelation velocity through a DLA mechanism leads to unwanted "loose and expanded" gels.

In turn, the effects of earth alkali salts on the advantageous middle-modulus water glass were theoretically assessed using the DLVO theory. Thereby it is possible to effectively reduce the energy barrier of the water glass sol through earth alkali salts with solubility of around L = 0.02 mole/l (bivalent cation). The temporal progressions of the rigidity and firmness development of various formulations of silicate binders with different earth alkali salts as additives were tracked using ultrasonic measurements, corroborating the considerations based on the DLVO theory that lower solubility generally results in slower setting. The results led to calcium sulphate as a chemical additive in the form of an anhydrite with solubility of around 2.7 g/l in water. This "neutral salt" (designated as gelation initiator GI) does not raise the pH value of water and effectively reduces the calculated value of the energy barrier of the middle-modulus water glass.

Generally, this results in various interactions and a process sequence for the significant reactions with layer formation from the initial components {middle-modulus water glass, quartz powder additive QM, and gelation initiator GI ($CaSO_4$, AII)} – sketched in Figure 2 with I to V [9].
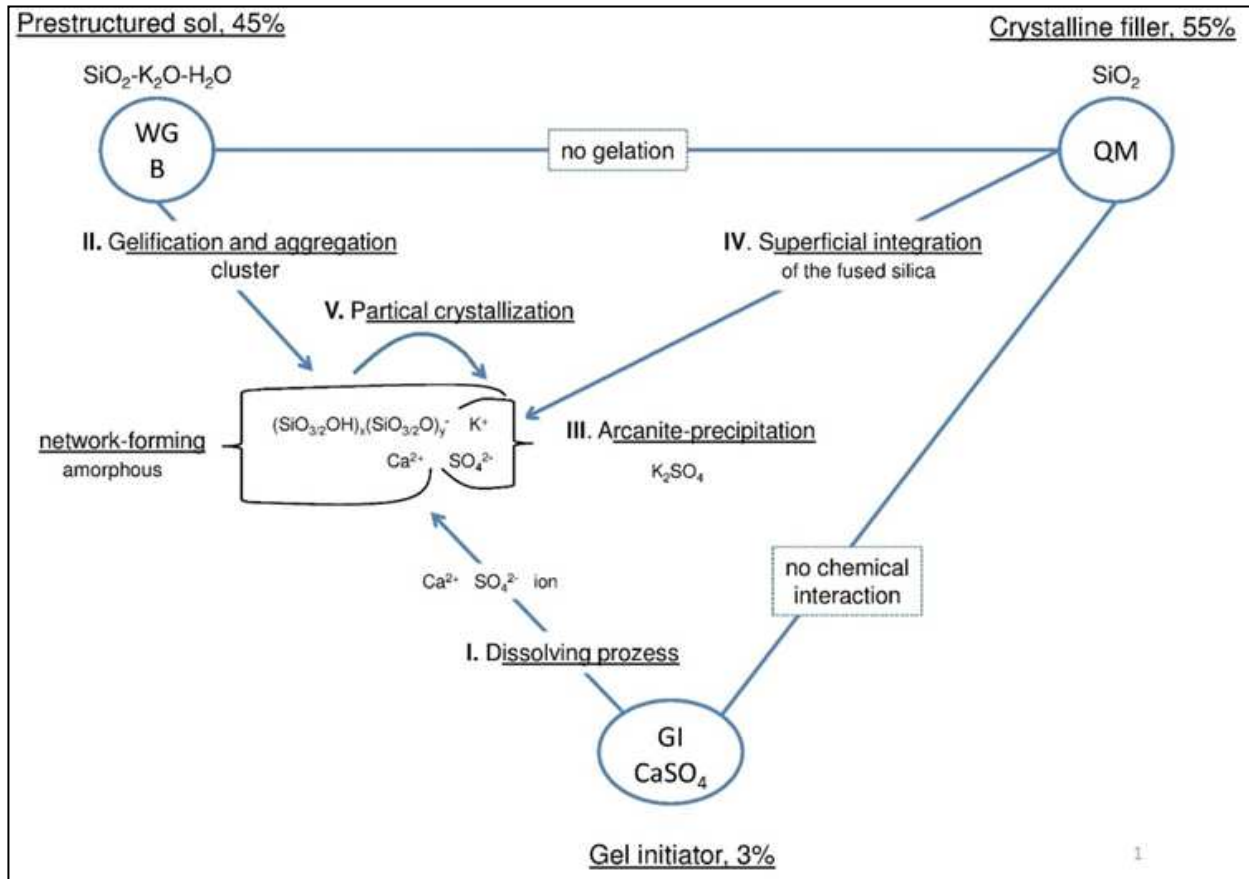
Figure 2: Components and their interactions with layer formation

In the long-term research of layer materials (from water glass, quartz powder additive, gelation initiator GI) at a coating thickness of d ≈ 5.0 mm on a roughened carrier plate (fibre-cement plate) in a bond, sufficient mechanical strength already developed after one day for the middle- and high-modulus water glass. While the silicate layer of the middle-modulus water glass remained crack-free, the layer with high-modulus water glass, where the DLA characteristic of a too-fast aggregation was more pronounced and silicate particles of too large size were initially present, the crack formation was as expected. The coatings of both these water glasses are, contrary to the lower-modulus water glass, durable and did not show any significant change with bonded storage at an alternating climate (for around 1 year). At restricted coating thickness of d ≤ 5.0 mm, the developed shrinkage stresses were lower than the maximum stress of the silicate layer material consisting of middle-modulus water glass (RLA mechanism). The extent of the shrinkage was at around 5% with the sole use of quarzitic filler material. The silicate coating with the middle-modulus water glass could be reproducibly produced on a fibre-cement plate; it was durable and reached surface hardness of 70 Shore-D already after one day. The water resistance develops within the first 12 days with coating thickness of around 5 mm and processing time of around 7 min. This period can be shortened to 2 days through modest

heat treatment in the range of 80 to 100°C. The flexural strength of the coating material, measured at a prism (4*4*16 cm^3), amounted to 10 N/mm^2 after 28 days and the compressive strengths to 27 N/mm^2 (high-modulus water glass: flexural strength = 5.2 N/mm^2; Compressive strength =13 N/mm^2).

For coating materials with the low-modulus water glass, disadvantageous occurrences such as late crack formation and salting and sweating-out effects as a result of drying and progressive carbonation of the initially stabilising KOH could be readjusted under the above-mentioned conditions. These occurrences can be traced to pronounced maturation processes, where the silica species cluster together over an extended period of time to form compact silicate networks. The cause of the disadvantageous and late occurrences was the starting presence of too-high monomer amounts in the initial water glass and thus the insufficient pre-structuring of the low-modulus water glass, which caused the gelation initiator GI to be insufficiently effective. Furthermore, larger amounts of K$_2$O are necessary to stabilise the high monomer content in the initial water glass. The higher K$_2$O content initially preserves the pronounced electrostatic stability, which counteracts the compression of the silicate network after the gel point. This stability of the water glass is only slowly reduced by carbonation of the K$_2$O amount, which causes the compression and maturation processes to take place over several months under outdoor climate conditions (moist-dry storage). In the sequence of these processes, the surface initially rigidifies through evaporative effects. The still "softer" silicate material below the surface is incapable of absorbing the shrinkage stresses resulting from the rigidifying surface. This leads to formation of the first cracks after around one month. Through further compression of the network, the rigidity over the cross-section increases. However, the water content also decreases at the same time through drying processes in the water glass below the surface. The water glass, which is now present at the surface through the contraction of the silicate network as a result of the drying processes and the carbonation of the stabilising KOH at the surface, immediately dries and gelates. After around 70 days, this leads to more pronounced sweating of salts. Now, the tendency to form cracks decreases again due to the tensile strength that has developed.

6. Deductions for aluminosilicate binders

For the silicate materials, potassium water glass with molar ratio of 2.9 was used to generate early-compact silicate networks. This water glass solution is characterised by its appropriate pre-structuring and number of silica species depending on the molar ratio and the substance amount concentration.

Aluminosilicate binders (geopolymers) are generally formed by adding additional soluble solid components such as metakaolin or fly ash into the water glass solutions (fresh-paste suspensions). It is only possible to reactively introduce the Al_2O_3 components into the binder network in this way through a sufficiently pronounced dissolution process. In turn, this required highly alkalic water glass solutions with pH values larger than 13 or with molar ratio lower than 2.5. As such, the dissolution potential of water glass solutions – in relation to the solid matter powder – proves to be another significant prerequisite for the production of aluminosilicate binders that can be usable in practice. In addition, the sufficient pre-structuring of SiO_2 components in the water glass solution appears to be distinctly beneficial to good binder performance. As is generally known, a water glass solution is only then sufficiently described in its chemical composition and structure, if aside from the molar ratio further information is provided on the content or concentration of one of both components SiO_2 or K_2O. Figure 3 shows the composition, molar ratio, and SiO_2 molality of the potassium water glass solution with which aluminosilicate binders are produced by using metakaolin and fly ashes [10]. For comparison, the composition of low, middle, and high-modulus water glass solution has been added from tests of silicate binders (Chapter 5).

Various amounts of 50% KOH solution have been added to a water glass stock solution (molar ratio = 2.92), lowering the molar ratio and SiO_2 molality to ranges significantly lower than that of middle and low-modulus water glass solution (upper picture figure 3). At the lower part of Figure 3 it can be seen that the pH values rise above 13.0 and the A_O/A_M values for pre-structuring according to HUNT et al. [8] are at 5 to 12.

These conditions produce stable, water-resistant aluminosilicate binders that turn into sulphate-resistant concretes by adding aggregates (prism 4*4*16 cm^3: 5-d compressive strengths in the range of 45 to 60 N/mm^2) [10].
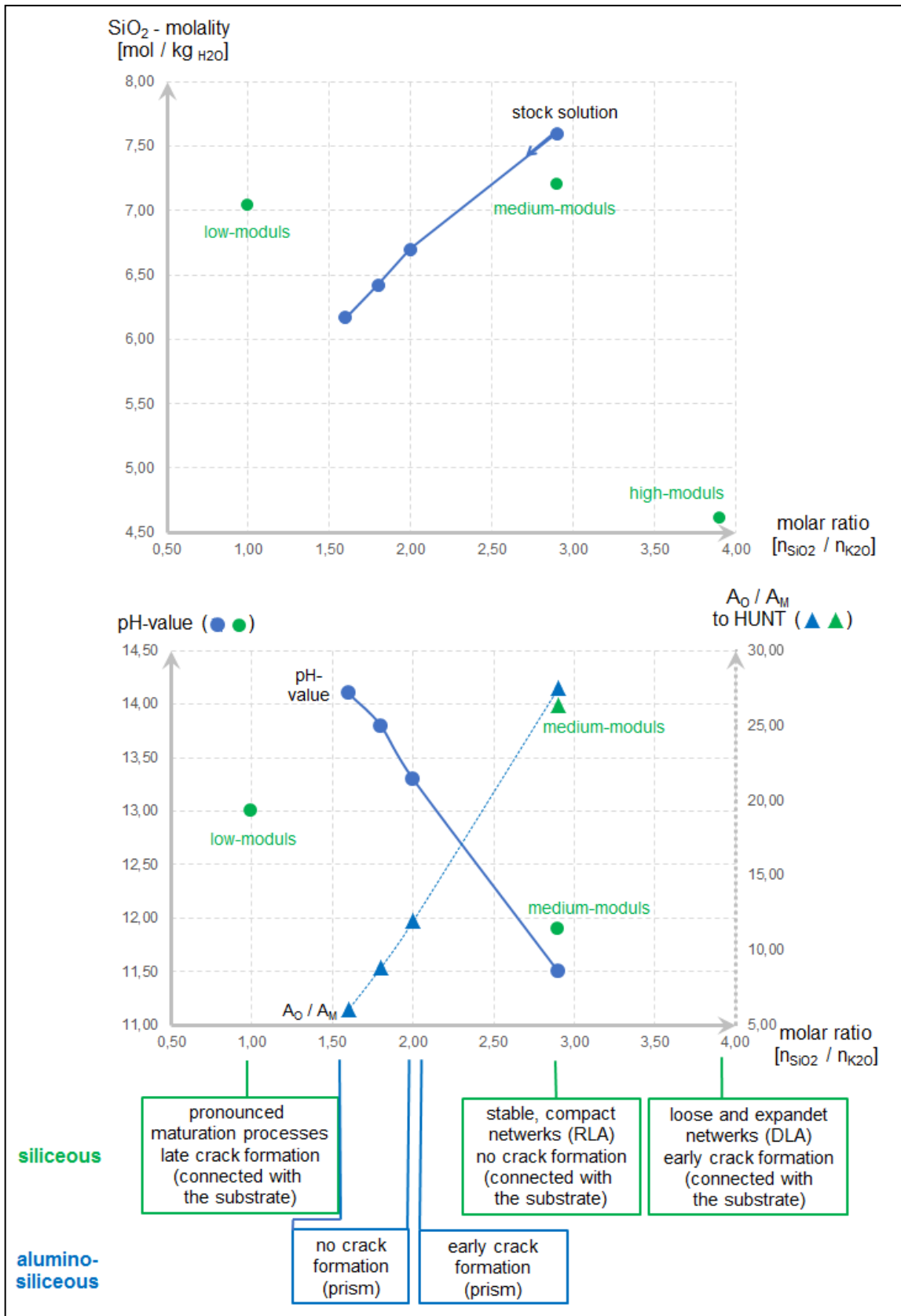
Figure 3: Potassium water glass solutions represented by the molar ratio and SiO_2-molality (above); pH value and A_O/A_M ratio (below) as a measure for the pre-structuring for silicate [2] and aluminosilicate [10] binders

Practical problems limit the operational areas of both types of binder: corrosive water glass solutions at molar ratio < 1.6 (relative to the technical regulations in occupational safety and maturation processes) and pronounced early crack formation in the binder (stresses as a result of diffusion-limited aggregation to larger silicate colloid and to enlarged water-containing alumosilicate networks).

The aluminosilicate binders were tested for water resistance and early crack formation with freely deposited prisms ($4*4*16$ cm^3). The following considerations should be taken into account in the further research on the long-term behaviour of aluminosilicate binders. The theoretical and experimental assessment of the aggregation process and thus the evaluation of the compactness of the aluminosilicate network, which has formed after the sol-gel transformation, are not easily estimable by using the DLVO and percolation theories because of the presence of additional Al_2O_3 and – in certain cases – CaO components, nor can they can be assessed with measurements of the gelation velocity and rigidity. Furthermore, contrary to purely silicate water glass binders, the aluminosilicate networks contain additional fixed negative $AlO^-_{4/2}$ charges, components which do not contribute to continued condensation and bind potassium cations, thus having a stabilising effect. Therefore, with the production of aluminosilicate binders, the network that is created needs to be experimentally assessed with respect to the further densification processes after the gel point. Here, as regards the durability of the aluminosilicate binders, the aspects of maturation and aging processes are of importance, particularly when testing the long-term behaviour under environmental conditions.

The aluminosilicate materials produced can show minor shrinkage and sufficient water resistance in the first days and weeks after the sol-gel transformation and the subsequently increasing stability. This is because the K_2O still present after gelation counteracts the densification of the aluminosilicate networks. However, through slowly progressing carbonation of K_2O and thus the reduction of the electrostatic stability due to a decreasing pH value, the created aluminosilicate network continues to densify through further cycles as a result of damp and dry storage. These processes are very slow, depending on the environmental conditions (months to years), and in case of exceedance of the maximum stress levels can lead to late crack formation or in the case of free storage - to the reduction of the mechanical properties. These late crack formations or stability degradations are critical, as they take place at a moment when such binder systems are potentially no longer subject to assessments.

The testing for late crack formations and thus assessing the durability of such aluminosilicate binders through free water storage, with which chemical equilibria set in, exerts no force and also counteracts carbonation. It is, therefore, a less suitable method, whereby weathering effects can only be measured through back weighing. The same applies to the exclusively dry storage. To test the durability and thus the functional capacity of such aluminosilicate materials regarding

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later maturation processes, the bonded material – thus under pressure – should be raised onto a sufficiently roughened carrier plate, for example from concrete, in layers of one to a few centimetres. To put into effect the deformation resulting from the maturation processes through stresses over the cross section, the carrier plate needs to be of the appropriate thickness and therefore stiffness / deformation stability. The assessment should take place in a dry-moist alternating climate, to allow for the carbonation of the stabilising K_2O and reorganisation and thus densification of the network under alternating dry-water stress. The testing period should exceed one year.

The number and sizes of the silica particles in the water glasses as well as the mechanism of the initialised aggregation processes are of crucial importance for durable, silicate, and crack-free binder materials. In addition to these parameters, a sufficiently effective dissolution process needs to be facilitated for the aluminosilicate binders. Thereby, aside from the initial properties such as water insolubility, early crack formation, gelation velocity, rigidity development, mechanical properties etc., above all the durability should be assessed and evaluated over an extended period of time.

7. <u>Literature</u>

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