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Silicate coatings for concrete components with waterglass systems by means of neutral salt initiation

1. Colloid formation and sol-gel transition in waterglass solutions

As early as around 1950, publications appeared describing and/or correlating the turbidity appearances and increasing viscosities of "aging" alkali waterglass solutions with the aid of the advanced light scattering measurement technology and establishing a relation to the formation of colloidal particles In "filtrated" sodium waterglass solutions with increasing waterglass module, particles with molecular weights of up to 10.000 (molar module 3.75) were found [1]. What is particularly remarkable is that a work by BRADY and employees [2] on potassium silicate solutions, besides the acid-initiated (pH value reduction by addition of acid) "polymerisations", also quantitatively describes the formation of colloid particles activated by neutral salts such as KCl and K_2SO_4 and compared it with "gel time" studies. For the formation speed, an exponential dependence on the concentration of the added salts was found (4th power). In comparison with the acid-initiated particles, the colloids produced by salt addition were not as large and/or voluminous (more densely packed where appropriate).

As is generally known, such colloid formations in waterglass solutions can lead to macroscopically observable sol-gel-transitions which are due to the increasing formation from condensable silanol groups in case of acid additions (1) and finally show - according to simple viewing - result in flexible network structures with gel properties by condensation polymerization (2).
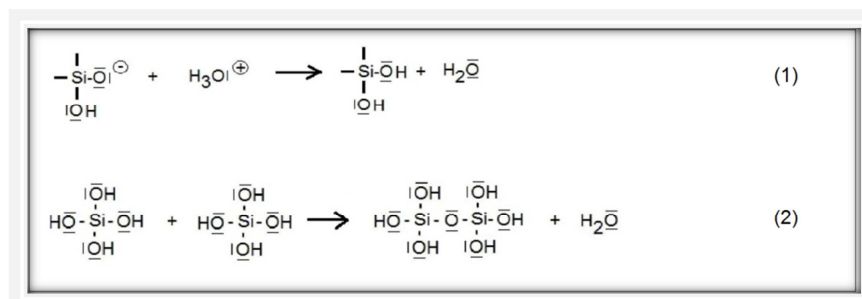
In the case of neutral salt additions, the potential barrier stabilizing the colloidal system in the electrostatic double layer around the particles (according to the DLVO theory [3]) is first of all reduced by the presence of dissolved salt ions (electrolyte [4, 5]) which has the result that the particles can approach each other more within the scope of the thermal movement. This way, a "reactive" proximity for the condensation of the silanol groups that are already existing in the waterglass sol is created. Double-charged cations of salts are more effective here than single-charged alkali ions and their distinct effect on the potential reduction increases with the concentration of the dissolved salt. The condensation reactions are more complex in the neutral salt initiation than those in the acid-initiated initiation, since additional hydrolysis and cation exchange reactions must be considered [6].

In the technical and/or construction-chemical practice for the use of the binder effect of alkali waterglasses the initialization by acid admixture (mineral acids, diacetate and triacetate, dihydrogen and cyclo phosphates, CO_2 fumigation) has been preferably used until today, since the gelatinization proceeds relatively quickly. In general, the material bound this way silicatically is not very stable because a relatively high quantity of free water is bound in this method of production of the networks, which has adverse effects in particular in case of larger material thicknesses ("sweating" of water and alkaline salts).

The objective of the investigations was the proof of the application possibility of the principle of neutral salt initiation of the protecting silicate coating of concrete components, e.g. of finished factory parts or reinforced concrete components, by showing useful coat properties and relevant reactions in the coat formation. The selection and/or determination of suitable initial components were the essential condition for that:

  a) Waterglass solution (WG): suitable module and concentration for an optimum prestructuring (medium- to high-module), low efflorescence

  b) Gel initiator (GI): Neutral salt with sufficient solubility in watery alkali silicate systems, type MX with "colorless" M^{2+} cations

2. Coating and coat properties

In the investigations, the silicate coatings were carried out on Eterplan fiber cement plates (manufacturer Eternit, thickness 1 cm), and it should be possible that they have a thickness of up to 5mm in the application case. It was the objective to produce coats that are free from cracks and efflorescence, stable, adhering firmly to the model floor plates; for the slurry to be applied, processing times of about 3 to 15 min were to be guaranteed. The coating material contained three components:

- Waterglass solution (WG)
- Quartz flour (QM)
- Gel initiator (GI)

For the optimum homogenizing of the mixture, the fused silica and the gel initiator (fine-grained neutral salt) were mixed first of all and then uniformly introduced into the waterglass solution by stirring.

The coating material was applied manually on the concrete slabs. To determine a suitable potassium waterglass, three waterglass solutions with a different module were used. Table 1 contains essential parameters of the used waterglass solutions of the system K_2O-SiO_2-H_2O.

Table 1: *Key figures of the used potassium waterglass solutions (WG)*

Parameter	WG A	WG B	WG C
Molar module SiO_2/K_2O	3.9	2.9	1.0
Solids content [%]	28	40	52
Density [g/cm^3, 20 °C]	1.25	1.40	1.64
pH-value	11.4	11.9	13.0

The watery alkali silicate sols, that is waterglasses and/or waterglass solutions/sol, are object of research in silicatic and the alumosilicatic binders (geopolymeres). Component of this work are silicatic binding agents. Unlike the geopolymeres, no dissolving reactions of solid alumosilicatic basic materials (meta clays) are necessary here, and therefore, waterglass solutions with pH values of less than 12 can be used. The waterglass WG C is classified as a caustic chemical and was only used for comparison purposes.

Figure 1 shows the experimentally determined viscosity process of the waterglasses - at first by acid gel initiation - after addition of various quantities of triacetin ($HC(Ac)(CH_2Ac)_2$ + 3KOH$\rightarrow$ 3KAc + $HC(OH)(CH_2OH)_2$, where Ac = acetate = $CH_3{}^.COO^-$).
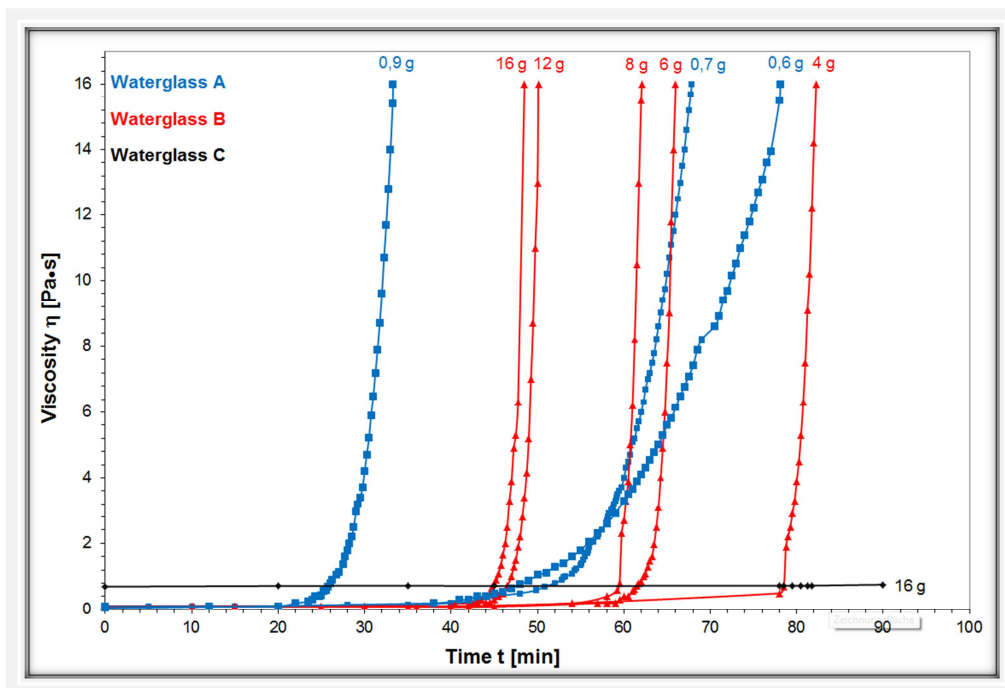

Fig. 1: *Viscosity increase in potassium waterglass solutions (WG A, WG B and WG C)*
by acid initiation by means of triacetin addition (triacetin volume per 100 g WG)

The high and/or medium-module waterglasses WG A and WG B reveal a noticeable viscosity increase within 80 min after added volume-dependent times, which is the expression of a beginning sol gel transition. With up to 20 g of triacetin, no viscosity increase is detectable in the low-module waterglass WG C, even up to times of about 180 min.

Because of the usefully variable time for the beginning of the gelification of the waterglasses WB A and WG B of between 30 and 80 min, these two waterglasses were used in the further investigations.

Figure 2 shows the effect of neutral salt additions on the gelification behavior in mixtures of the selected waterglasses WG A and/or WG B with fused silica QM (average particle size: 31 µm, max. particle size: 125 µm).
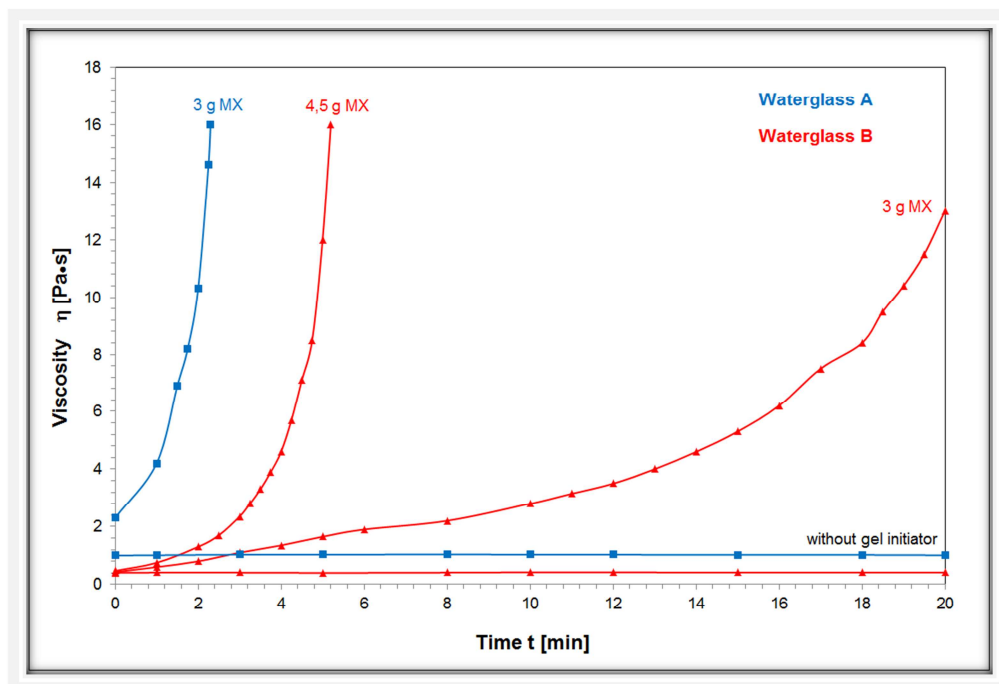

Fig. 2: Viscosity development in mixtures of potassium waterglass solutions
WG A and/or WG B and fused silica (45 g WG, 55 g QM) by neutral salt addition MX

The added gel initiator salt MX is an anhydrous calcium sulfate ($CaSO_4$) that initiates viscosity increases in the WG-QM mixtures that are comparable with those of triacetin (see Figure 1).

Without salt addition, the viscosities of these mixtures remain demonstrably unchanged below 1 Pa·s in the measurement period (20 min). By means of the added salt quantity (3 bis 4.5 g), waterglass WG B facilitates a useful setting of the beginning of the sol gel transition (optimization of potlives), whereas WG A gelatinizes too quickly.

The development of a certain stiffness in a mixture of waterglass WG B and the fused silica QM after addition of 3 g each of different neutral salts of type MX is shown in Figure 3 at the measurement of the velocity of sound in the mixtures.
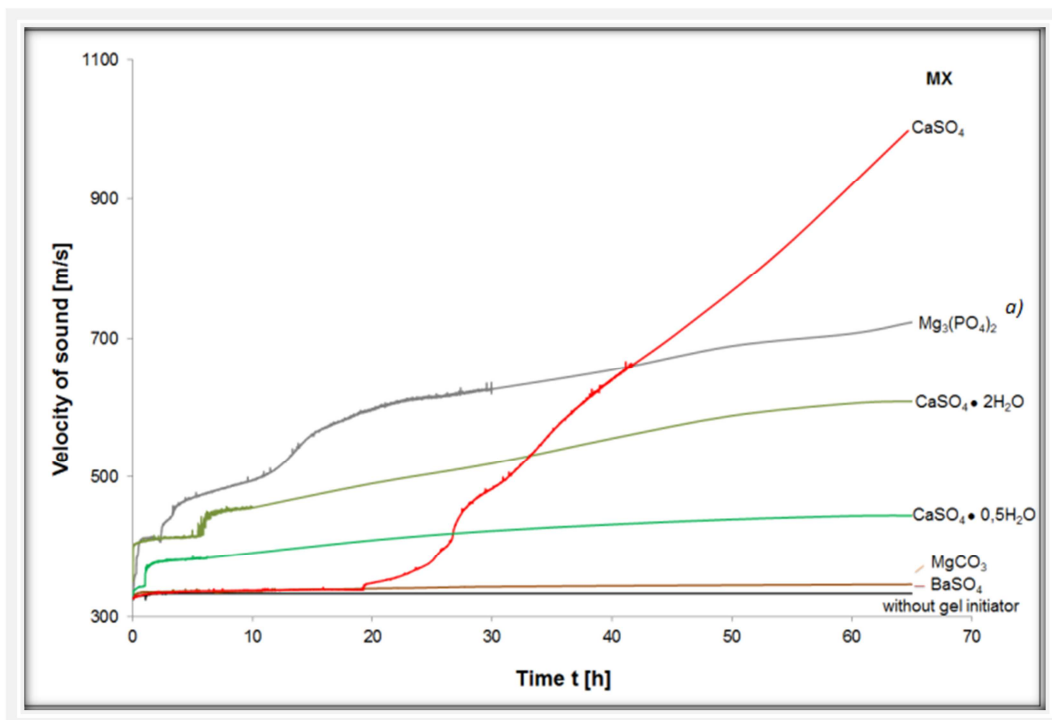
Fig. 3: Stiffness development in WG B - QM mixtures (45 g WG, 55 g QM) after addition of various alkaline earth salts (3 g), characterized by measurement of the velocity of sound in the material; a) additional: $Mg_3(PO_4)_2$ and $MgSO_4 \cdot 7H_2O$, $Ca(OH)_2$, BaF_2, $(NaPO_3)_3$ in PhD thesis Kai Schuch

According to the DLVO theory, the effect of the gel initiator salts is strongly dependent on the solubility of the electrolytes (concentration of solved ions). In the WG-QM mixtures, the very differing dissolving behavior (time dependence of the dissolving process) obviously takes effect with regard to the stiffening behavior.

While $BaSO_4$ and $MgCO_3$ have a too low solubility in the mixtures and do not reveal virtually any appreciable effect up to 65 h, the calcium sulfate variants cause a noticeable increase in ultrasonic velocity (stiffness) in the WG-QM mixtures. At the beginning (up to 5 h), the measurement curves of the hydrated calcium sulfates Gips ($CaSO_4 \cdot 2H_2O$ and hemihydrate $CaSO_4 \cdot 0.5H_2O$) show "jumps" that are probably caused by local agglomeration effects (lump formation), remain in times of up to 65 h in a low area of the measured values, however, which is why no technical use in coating systems is to be expected for these gel initiators. The anhydrous calcium sulfate $CaSO_4$ is an anhydrite II and is characterized by a steep increase in stiffness in the effect in the WG-QM mixture which has a positive effect and begins after about 20 h. Up to this time, such a coating material can still emit sufficient volumes of evaporable water.

The suitability of the waterglass WG B as a silicatic basic system is also proved by light microscopic pictures of coatings on fiber cement plates in comparison with WG A and WG C in Figure 4. The following base formulation was selected: 45 g WG B, 55 g QM and 3 g GI $CaSO_4$(AII).
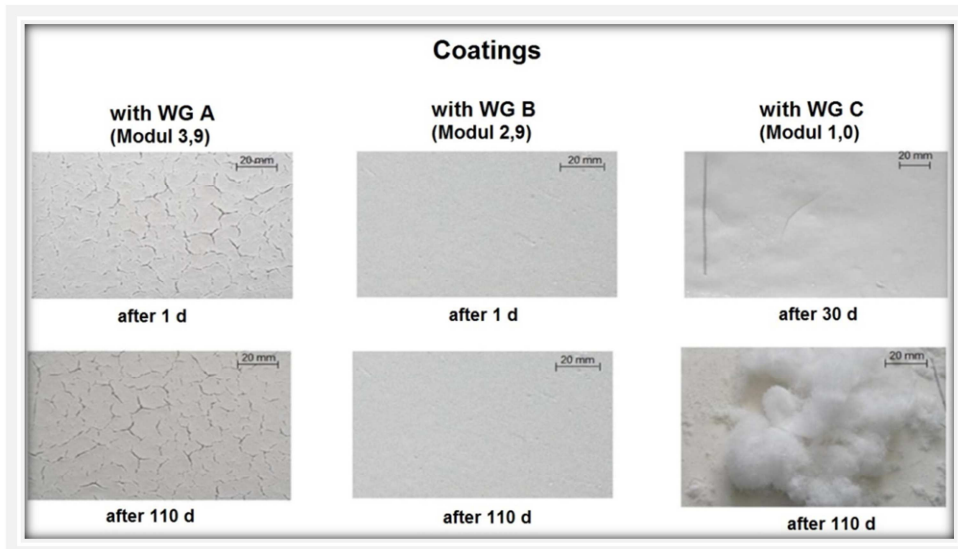
Fig. 4: Coatings (thickness about 0.4 cm) on fiber cement plates after 1 and 110 days in laboratory atmosphere

The coats with the WG B are characterized by a firm adhesion on the fiber cement plate while the coat with WG A due to too fast gelification with water inclusion (refer to Figure 2) already shows a marked cracking after 1 day and the coat with WG C shows noticeable efflorescences (voluminous salt efflorescence) due to insufficient networking and/or incomplete aggregation and high alkali contents after 110 days; the latter coatings do not reach any appreciable solidification in the investigation period, either (see scratch lines).

The mechanical characteristics of the silicatic coating material according to the base formulation with WG B are exemplarily displayed in their chronological development in Table 2. The strengths and the shrinkage values were investigated at standard prisms ($4 \times 4 \times 16$ cm^3) and the shore D hardness at plates (d= 5.7 cm, h= 0.5 cm, test device manufacturer Zick) after storage in laboratory atmosphere (20 °C, 65 % r. h.). For comparison, the values of the coat material with WG A have been added.

Table 2: Mechanical characteristics of the coat materials (base formulation with WG B and WG A)

	Flexural strengths [N/mm^2] after	Pressure strength [N/mm^2] after		Shore-D-hardness after		Shrinkage values [%] after
	28 d	28 d	450 d	3 d	28 d	60 d
with WG B	10.0+0.4	26.9+0.8	29.8+0.9	85+3	93+4	5.5
with WG A	5.2+0.4	13.3+0.5	14.7+0.5	58+2	80+3	7.9

The strengths are almost fully developed after 28 days and are about twice as high with the coating material with WG B as with that with WG A. Related to the detected pressure strength, both waterglass-based materials prove markedly high bend flexural strengths. The measured values are almost three times as large as they would be expected according to general findings in the case of a cement stone and/or cylindrical grain concrete [7, 8]. After three days already, a shore D hardness value is reached

that is specified as final hardness for epoxy resin coatings on concrete floors [9]. With a shrinkage value of 5.5 % (60 d) a relatively high shrinkage measure is found that is about the tenfold of a cement paste [10]. The investigations show, however, that coatings with WG B in the base mixture are possible crack-free and without debonding from the fiber cement plates (see Figure 4), which suggests a sufficient adhesion and the ability of the WG B QM-based coats to absorb tension (structural elasticity). The tension buildup across the coating cross section (free and firm edge) does not lead to a transgression of the tensile strength here. Another reduction of the thickness by the application technique, e.g. putty knife technique, facilitates an additional reduction of shrinkage tensions and thus a further increased safety of use.

The effectiveness of the gel initiator in the coat formation process becomes obvious by the chronological development of the surface hardness according to shore D and the water resistance of the coating material in the form of cylindrical samples (panels with d= 5.7 cm and h= 0.5 cm) in the laboratory atmosphere. In Figure 5 these are shown with and without GI $CaSO_4$ (AII) in the coat material of the base mixture.
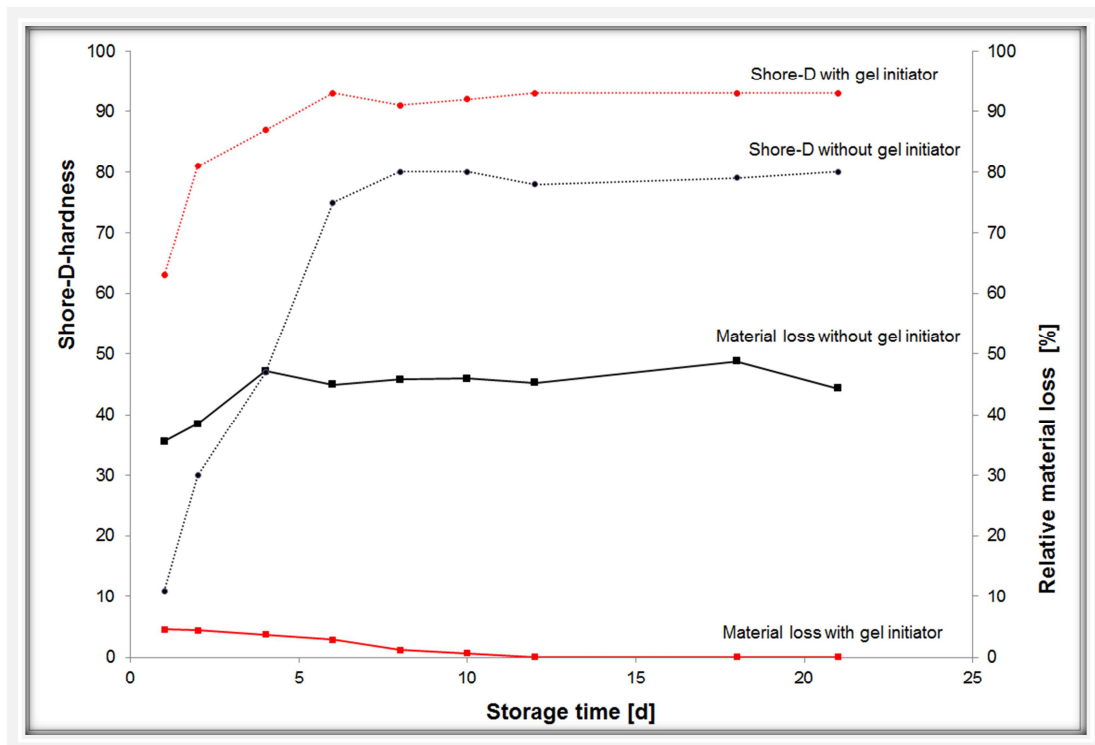

Fig. 5: Chronological development of the shore D hardness in laboratory atmosphere and the gravimetric material loss of the base mixture with inclusion of water (250 ml H_2O, 1 h; 100 °C drying, 4 h and correction of the additional drying loss in parallel measurements), gel initiator $CaSO_4$ (AII)

In particular in the initial phase of the coat formation (1st to 6th day), the gel initiator $CaSO_4$ effects a sufficiently high hardness that is reached by the suitable initialization of the silicatic base formulation (cf. Figures 2 and 3). Also, the gel initiator $CaSO_4$ facilitates a continuously increasing water resistance over time that can virtually be considered as fully developed after 12 days with a measure loss of < 0.1 %. Without gel initiator $CaSO_4$, the WG-QM base mixture does not achieve any water resistance even after 21 days of storage time in laboratory atmosphere (rel. mass losses around 45 %).

3. Essential reactions of the components WG B, QM and GI CaSO$_4$ (AII) in the coat formation

First of all, the material-structural state of the coats with base formulation after 20 days of storage in laboratory atmosphere (20 °C, 65 % r. h.) was characterized. The coat samples (storage thickness 0.5 cm) were crushed, milled and subjected to a differential thermoanalytic (DSC), an infrared spectroscopic (IR) and an X-ray diffractometric (XRD) diagnostic. Figure 6 shows the thermo-analytical picture (10 K/min) of the coat material.
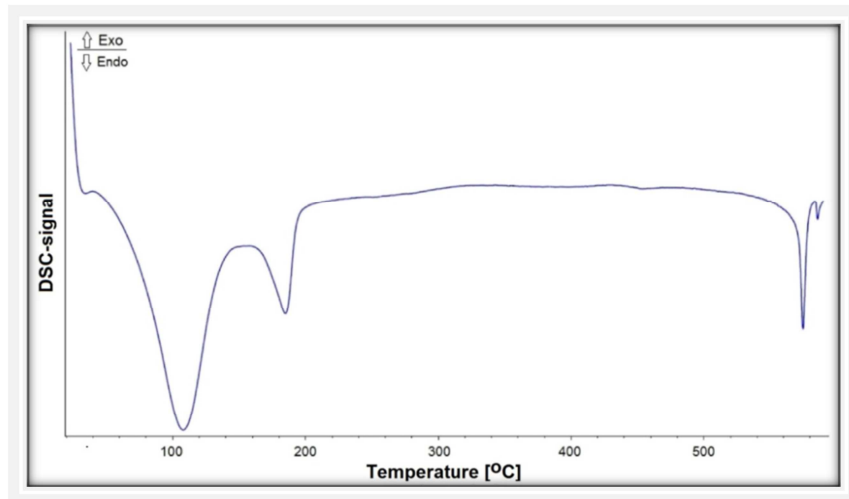

Fig. 6: DSC characteristic of the coat material (20 d)

The DSC curve proves the output of water (30 to 40 °C) from the surface and from the volume (80 to 130 °C) of the consolidated coat material. In the area around 190 °C the splitting of H$_2$O and CO$_2$ from the superficially formed KHCO$_3$ (carbonation in laboratory atmosphere) is to be expected. At 575 °C, there is a sharply restricted endothermic peak indicating a quartz jump similar structure transformation. An infrared spectrum of the coat material is shown in Figure 7 in comparison with that of the added fused silica QM.
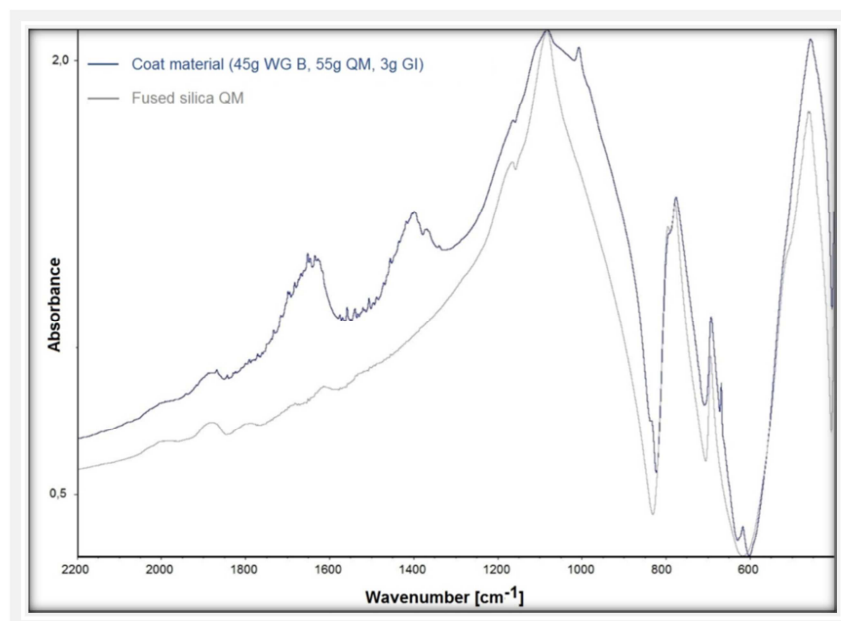

Fig. 7: IR spectrum of the coat material (20 d) in comparison with that of the fused silica QM

In the "fingerprint" range (400 to 2000 cm^{-1}) an extensive agreement of both spectrums is found. Characteristic for the spectrum of the coat material are the absorption bands of around 1630 cm^{-1} that are caused by deformation oscillations of water in hydrated quartz glass structures ($SiO_2 + H_2O$) [11] and of around 1380 cm^{-1} that are considered as carbonate and/or hydrogen carbonate bands due to carbonation of the alkaline coat material in contact with the CO_2-containing air of the laboratory atmosphere (20 d) [12, 13, 14]. The "shoulder" area of the IR spectrum of the coat material (about 850-980 cm^{-1}) which clearly sets itself apart from the gradient of the fused silica spectrum, should be related to the silanol groups (Si-OH) of the silicate network [15, 16].

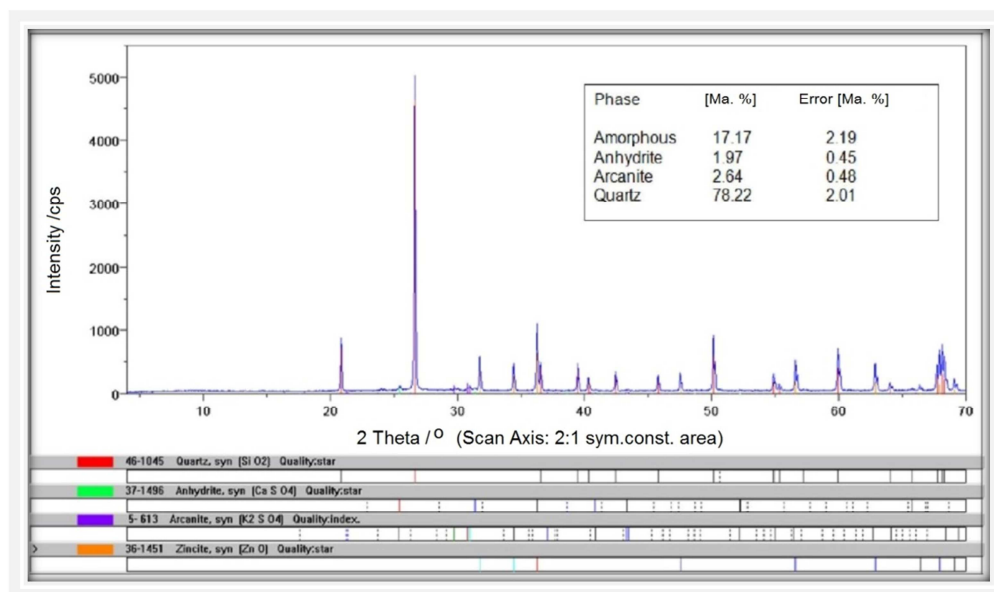The X-ray diffractogram of the coat material is shown in Figure 8.

Fig. 8: XRD recording of coat material (20 d) with ZnO addition as crystalline standard

As expected, the X-ray phase analyse shows quartz as a crystalline main component (SiO_2; 78.2 %), besides that, however, also arcanite (K_2SO_4; 2.6 %) and anhydrite ($CaSO_4$; 2.0 %). For the silicatic network in the coats, an amorphous part of 17.2 % is found.

To characterize the reactions between the three components of the base mixture during the coat formation, "time lapse" examination series were carried out. For an accelerated sped-up coat formation and forced dehydration, mixtures of different component combinations were subjected to a 12-hour heat treatment at 100 °C and then checked by means of DSC and XRD. A compilation of the differential thermoanalytical curves is displayed in Figure 9.

As expected, the waterglass WG B (Figure 9a) shows a surface and volume dehydration and besides a marked water output in the range of 450 to 500 °C that is probably due to combined water at the slightly aggregated waterglass (dehydroxilation of the extensive silanol groups). The endothermic effect at 575 °C (see Figure 6, quartz jump similar structure transformation) is not provable, that is, no formation of quartz-determined structures occurred during the 100 °C heat processing in the waterglass B.
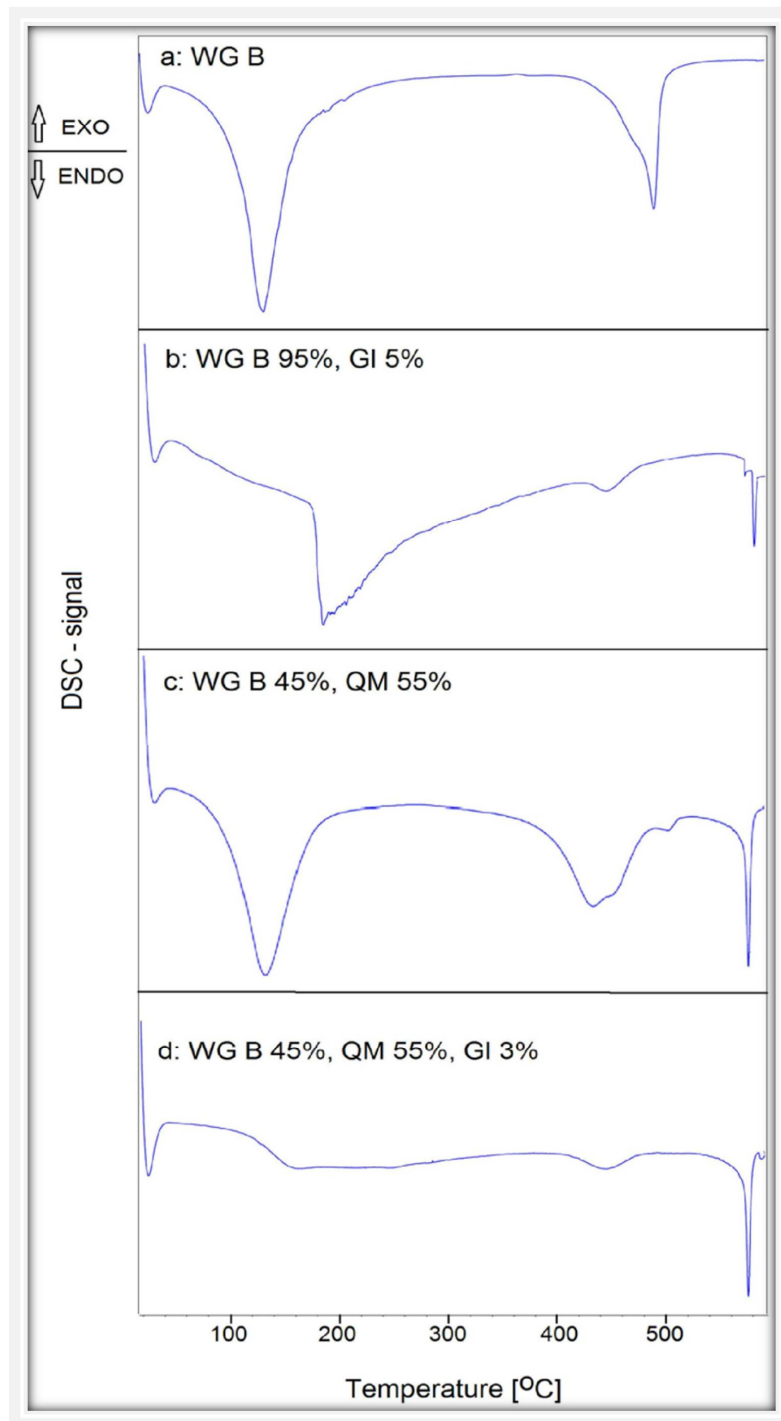
Fig. 9: DSC measurement curves of mixtures after heat treatment at 100 °C (12 h), "time lapse" preparation

When the gel initiator $CaSO_4$ is added to the waterglass WG B (Figure 9b) a sol-gel transition with subsequent network formation should be possible during the heat treatment. Due to the initiated network formation, the volume dehydration can only be observed with a delay at clearly higher temperatures of about 200 °C. The reduction of the measurement curve at 425 °C can be interpreted as a glass-transformation (Tg) of the amorphous potassium silicate network and/or a weak dehydroxilation (remaining silanol groups).

However, this recording already shows the sharply restricted endothermic peak for a structure transformation of quartz-similar components that have obviously formed from the condensed silicate network by partial crystallization on condition of the heat treatment of the WG B under the gel initiator effect at 585 °C (without QM addition!).

The thermoanalytical curve of the mixture of waterglass WG B and fused silica QM (Figure 9c) shows with the dehydrations at 30 to 40 °C and 100 to 180 °C as well as a noticeable dehydroxilation at 380 to 460 °C as well as the structure transformation of the added fused silica at 575 °C that no noteworthy reaction occurred between both components.

Finally, recording of the three component base mixture (WG B, QM and GI, Figure 9d) in the "time lapse" preparation proves a stable coat material formation in the form of a silicate network (glass transformation at 420 °C) with fused silica filling (quartz jump at 575 °C). Apart from that, no major dehydration (apart from surface water) can be found in this measurement which indicates a successful water discharge from the silicate network in the "time lapse" preparation (100 °C).

The remarkable result of the "time lapse" examinations that the gel initiator $CaSO_4$ the waterglass WG B alone without fused silica addition leads to crystalline quartz portions in the silicate network, is also provable by an X-ray diffractometric phase analysis. Figure 10 also proves 1.3 % quartz for this sample besides the amorphous part of the silicate network of 89.1 % and 9.6 % arcanite.
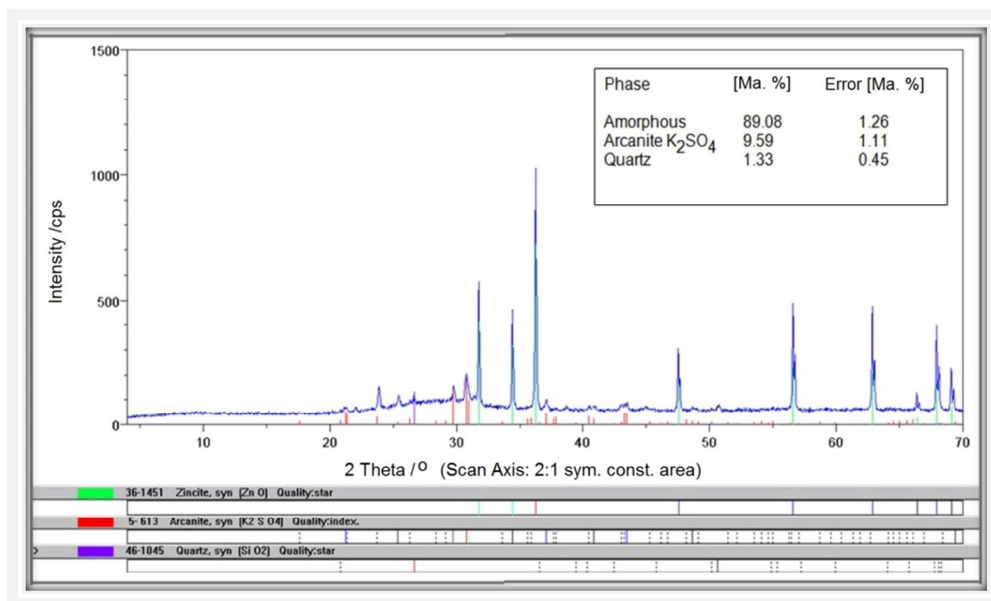

Fig. 10: XRD recording of the "time lapse" (WG B 95%, GI CaSO₄ (AII) 5%) sample with ZnO addition as crystalline standard

Altogether, a process sequence that is outlined in Figure 11 results from the initial components waterglass WG B, fused silica QM and gel initiator GI ($CaSO_4$, AII) for the essential reactions in coat formation.
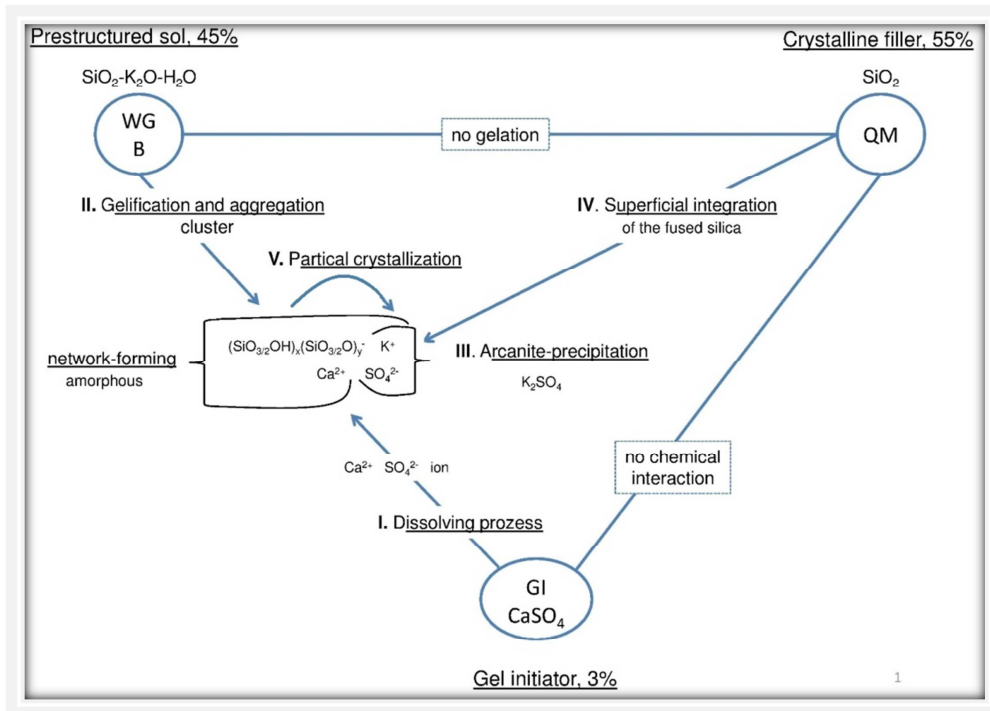
Fig. 11: Components and their interaction in the coat formation

The chronological sequence of the chemical reactions and construction material processes is shown in the material triangle WG B-QM-GI by the steps I to V. The start processes (I, II) are on the GI-WG B axis - starting from the GI gel initiator. A formal classification into the application-technological procedure of the coating (without heat treatment) is provided in the following overview.

3.1 Coating

- Mixture homogenizing of the fused silica QM and gel initiator GI
- Input of the QM GI mixture into the waterglass WG B (stir in)
    (I) dissolving process of the gel initiator GI ($CaSO_4$, AII) while emitting the ions Ca^{2+} and SO_4^{2-}
- Application of the suspension (WG B, GI and QM) on the concrete component
    (II) gelification and aggregation of the waterglass WG B (reduction of the potential barrier) while forming an amorphous silicate network
    (III) Precipitation of the crystalline by-product arcanite (K_2SO_4)
- Coat formation (solidification while forming a technically more usable shore D hardness)
    (IV) superficial integration of the fused silica particles via silanol groups of WG B
    (V) Partial transformation of the amorphous silicate network into quartz-similar structures (partial "quarzitic formation")

4. Summary and conclusions

The objective of the investigations was the proof of the use of the neutral salt initiation as a construction material in the protecting silicate coating of concrete components factory finished parts or reinforced concrete construction parts, by means of waterglass fused silica suspensions.

As a gel initiator GI in a potassium waterglass (molar module $\approx$ 3, pH-value $\leq$ 12; WG 45 %), anhydrite ($CaSO_4$, AII; 3 %) facilitates a fused silica (QM 55 %) mixture a suitable setting, so that practical processing times of up to 25 min can be set. The coating (4 mm thickness) shows already after 2 days a shore D hardness of more than 80, and a highly-efficient water resistance is given after 12 days. The final pressure resistance (27 N/mm^2) of the coat material is reached after 28 days. What is also remarkable are the relatively high bend flexural strengths (10 N/mm^2) that are measured at the silicatic coat material after 28 days that make it possible to achieve crack-free coatings that are firmly adhering to the concrete - even in case of noticeable shrinkage. The XRD analysis of the coat materials (28 d) displays 78 % quartz (preferrably from the QM), 17 % amorphous components (silicatic network), 2.6 % arcanite (K_2SO_4, by-product from WG and GI) and 2.0 % anhydrite (from GI).

"Time lapse" preparations (100 °C heat treatment, 12 h) from mixture combinations of the three basic materials WG, QM and GI prove an indication of essential reactions in the coat formation by means of thermoanalytical and X-ray phase-diagnostic characterizations. Via a dissolving process, the gel initiator $CaSO_4$ leads to the gelification and aggregation of the structured potassium waterglass solution (formation of a silicate network) and to arcanite precipitation (K_2SO_4), after which - besides the dominant amorphous part (silicate network) - small volumes of quartz (partial "quartzitic" formation) are already detectable. The fused silica used as a filling material does not act directly network-forming on the waterglass, but is first of all only integrated in the arising structure of the coat material via silanol groups (Si-OH) of the formed waterglass clusters.

Further investigations for the material-technological conversion of the silicate coating procedure with neutral salt initiation as well as details of the coat formation processes - in particular on the chronological sequence and the microstructural development - are necessary for further clarification.

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