

TIME-DEPENDENT DEFORMATION BEHAVIOUR OF SAP MODIFIED CONCRETE

ZEITABHÄNGIGE FORMÄNDERUNG VON SAP-MODIFIZIERTEM BETON

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ABSTRACT

Additives, consisting of cross-linked acrylic acid and acrylamide, known as superabsorbent polymers (SAP), were used in mortars and concrete to reduce shrinkage. So far, SAP have been used in great quantities for incontinence pads. In this medical application, SAP is able to absorb huge amount of water, urea, organic and inorganic salts like sodium chloride. The pH is in the range of 5 up to 8 – and nearly neutral. In opposite cement-slurries have a pH of 12.5 to 13.5 depending of the alkali-content. More sodium and potassium in cement lead to higher pH. The high pH value is a challenge for SAP's. 1. Super absorbers can assimilate significantly less water in the strongly alkaline environment than in the pH-neutral water and 2. Chemical degradation takes place over time and leads to the release of water. This behaviour is a desired effect. The internal curing delivers to a reduction of shrinkage in hardened concrete. Wet concrete in opposite starts to bleed. Water and cement slurry on the surface and between gravel and cement matrix reduces physical properties like compressive strength. Combination of SAP and stabilizer is the best way to optimize the performance.

ZUSAMMENFASSUNG

Additive, bestehend aus vernetzter Acrylsäure und Acrylamid, den so genannten Superabsorbern (SAP), werden in Mörteln und Beton als Schwindreduzierer eingesetzt. Als Inkontinenzeinlagen sind SAP's in der Lage großen Mengen an Wasser, Harnstoff, organischen und anorganischen Salzen wie Natriumchlorid aufzunehmen. Der pH-Wert liegt im Bereich von 5 bis 8 - und ist nahezu neutral. Im Gegensatz dazu haben Zementschlämmen einen pH-Wert von 12,5 bis 13,5, abhängig vom Alkaligehalt. Mehr Natrium und Kalium im Zement führen zu einem höheren pH-Wert. Der hohe pH-Wert ist eine Herausforderung für SAP's, da

sie im stark alkalischen deutlich weniger Wasser aufnehmen können wie im pH-neutralen. Hinzu kommt ein chemischer Abbau im Laufe der Zeit. Dies führt zur Freisetzung von Wasser und mit dem Resultat einer inneren Nachbehandlung des Betons. Die innere Nachbehandlung bewirkt eine Reduzierung des Schwindens im ausgehärteten Beton. Frischbeton mit SAP zeigt starkes Bluten. Wasser- und Zementschlämme zwischen der Gesteinskörnung und der Zementmatrix schwächen den Verbund und führt zu reduzierten physikalischen Eigenschaften wie Druckfestigkeit. Eine Kombination aus SAP und Stabilisator verhindert das Bluten.

KEYWORDS: Concrete, superabsorber, shrinkage reduction

1. INTRODUCTUION

In order to obtain meaningful results, several challenges have to be mastered. In advance, the manufacturer empirically determined the amount of SAP and additional water for optimal shrinkage reduction. The relationship between cement and SAP is defined on the one hand by the water-cement value but also by the cement itself (keyword: alkali content - pH value).

Target values for the fresh concrete must be adhered to so that the hardened concrete values are comparable. However, despite the increased water content, the SAP used leads to a strong stiffening of the concrete over time. The consistency should be almost identical for all concretes. If the concrete has a small spreading dimension, the reduced willingness to compact leads to increased air void contents and thus to reduced strength. To counteract this, superplasticizers based on polycarboxylate ethers are used. However, the use of polycarboxylate ethers with constant water content leads to a reduction in strength.

Normally, building materials based on Portland cement shrink after the addition of water. The reason is simple: The initial components (clinker phases and water) have in total lower densities than the hydrate phases that form [1]. If the building material additionally dries out, an even stronger shrinkage is observed. This is where the "simple" ends. Mathematical calculations usually lead to strong deviations in the comparison with the actual densities and volumes. In order to understand this discrepancy, it is necessary to look at the chemical and morphological processes. As hydrates of the clinker phases form, no well-ordered stoichiometric composition is observed, apart from a few exceptions such as ettringite. Rather, apart from not hydrated cement, phases with high H₂O contents are present. At

every place within the building material, more precisely the cement matrix, one has changing chemical compositions, which change strongly over time. These processes take place over years to decades. As, if this were not complicated enough, the secondary elements and the trace elements influence the hydration. Investigations by Chappex and Scrivener [2] show that the use of metakaolin in cements increases the incorporation of alkalis into the SCH-phases, while the H₂O content decreases.

Not only the chemical composition but also the habitus of the forming crystals plays a role in how strongly a cementitious building material shrinks. In the much simpler system CaSO₄-H₂O it is known that, with the addition of citric acid [3], tartaric acid and alkalis, the swelling behaviour can be reduced by a factor of 10 with simultaneous loss of strength. This becomes understandable when looking at the crystals under the microscope: When fruit acids are added to the mixing water, thick and short crystals form, while the crystals form long needles without acids. The density of CaSO₄*2H₂O crystals is identical in both cases. We can expect analogous processes in cementitious systems. If the cement contains e.g. high amounts of alkalis, which lead to a high pH up to 13.5 in the pore water, this will certainly also have an effect on the crystallization behaviour of all cement clinker phases.

When crystalline structures form, they grow together and lead macroscopically to strength. The contact points of the crystals occupy a key position. The better the crystals become raked and grow together, the higher is the strength. The behaviour of different retarders has been known for a long time. While polysaccharides destroy the strengths of concretes, phosphates lead to significant increases in strength after months. This finding has not been clarified yet.

In summary, the processes that lead to the shrinkage of cementitious building materials are due to chemical, mineralogical and morphological processes that are closely related to the chemical composition (relation of ions: Si⁴⁺, Al³⁺, Fe³⁺, H₂O, Ca²⁺, Na⁺, K⁺, SO₄²⁻, CO₃²⁻ and so on).

In order to reduce shrinkage, however, there are various approaches in addition to the mechanical ones such as swelling agents:

- a. Find the optimum ratio of ions that cannot pass into the gas phase and combine them to achieve the lowest possible density compared to the starting materials. Of course, there are narrow limits to this concept. For example, there are cement standards, but there are also chemical compositions that no longer have

much to do with Portland cement. Since this n-dimensional challenge (chemical, clinker-phase, granulometric composition, water/cement ratio, type and quantity of aggregates) is so great, it is not surprising that e.g. in publications authors partly come to diametrical results because it is impossible for all output parameters to match.

- b. The addition of shrinkage reducers has existed for a long time, which has also been reflected in standardization (EN 934-2). The name already indicates a shortcoming: With a shrinkage reducer it is not possible to prevent the shrinkage of cementitious building materials. Publications show a maximum shrinkage reduction of 50% [4].

If one looks at the chemicals that make up the shrinkage reducers, it becomes apparent that they are organic compounds with functional groups such as hydroxides, ethers and amines, which have a low vapour pressure.

The explanation favoured by many researchers that the addition of chemicals leading to a reduction of surface tensions [5] is due to the shrinkage behaviour of concretes and mortars can be ruled out for several reasons. Organic chemicals containing fluorine among other things reduce the surface tension extremely, but have no influence on the shrinkage behaviour. Furthermore, when concretes and mortars dry out, the number of partially filled pores decreases. Thus, shrinkage should occur at the beginning of the drying process. If the number of partially filled pores decreases significantly, the samples should swell again. One would have thus a shrinkage minimum, which was however never observed.

When chemicals are added for shrinkage reduction, two effects are decisive.

During the crystallization process, the organic foreign molecules influence the growth direction of the crystals and thus the crystal habitus by occupying defined crystal surfaces. Long needles should be better for strength and reduced shrinkage than short thick needles.

If the pore solutions contain organic molecules, these are partially incorporated into the structure of the calcium silicate and aluminate phases instead of H₂O molecules. The better these organic molecules fit into these crystals, the more is incorporated and the better these chemical compounds act as shrinkage reducers. During the drying process, the calcium silicate and aluminate hydrates lose part of their water and shrink. If, however, the hydrates contain larger amounts of organic molecules, these are held more strongly in the crystal structure. The crystals shrink less and so does the building material.

When using superabsorbers, two effects lead to the desired shrinkage reduction. The degradation of the polymer releases water and the degradation products can positively change the morphology and chemical composition of the hydrates.

2. RAW MATERIAL AND TEST METHOD

2.1 RAW MATERIAL

A CEM I 42.5 R was used (mineralogical composition according to Rietveld: C_3S 57.6 wt.%; C_2S 17.3 wt.%; C_3A 6.8 wt.%; C_4AF 8.6 wt.%). The round grain up to 8 mm comes from the upper and lower Rhine valley. The grading curve (AB 8 according to DIN 1045-2) was composed of four fractions. ViscoCrete VP 10160103 superplasticizer from Sika was used to adjust the consistency.

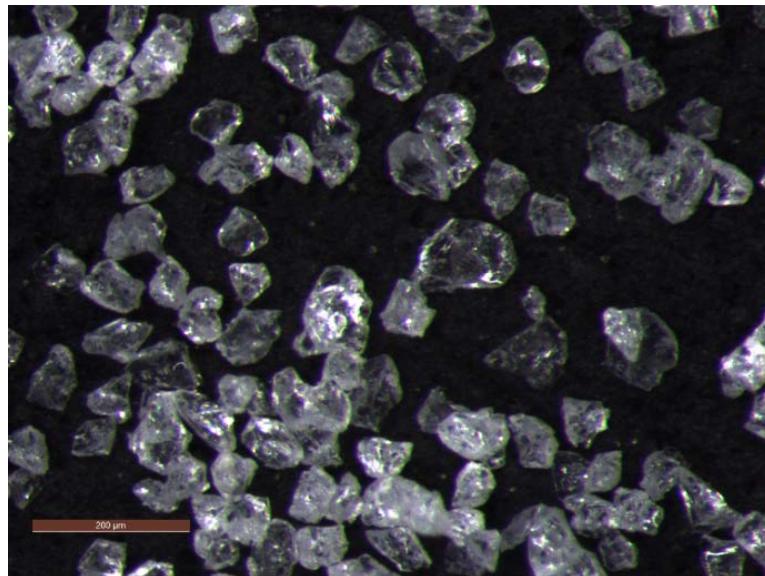


Fig. 1: Image of crushed SAP-particles produced by gel-polymerisation

BASF provided the used superabsorber (Fig. 1). The chemical basis of the stabilizer used is a natural polysaccharide. More than 60 mixtures have been made with the composition according Table 1.

Table 1: Composition in kg/m³ of the seven concrete mixture

	concrete without superabsorber			concrete with superabsorber			
	w/c-ratio	w/c-ratio	w/c-ratio	w/c-ratio	w/c-ratio	w/c-ratio	w/c-ratio
	0,36	0,42	0,5	0,42	0,42	0,5	0,5
aggregate	1796	1725	1629	1725	1725	1629	1629
CEM I 42,5 R	450	450	450	450	450	450	450
ViscoCrete VP 10160103	2,72	0,85	-	7,73	7,73	7,17	7,17
Superabsorber	-	-	-	1,17	1,17	1,58	1,58
stabilizer	-	-	-	-	-	0,02	0,02
water	162	189	225	184	184	221	221

2.2 TEST METHOD

Most of the fresh and hardened concrete tests were carried out according to the standards of the DIN EN 12350 and DIN EN 12390 series.

In order to be able to compare the concretes with each other, the recipes were adapted so, that consistency class F3 (DIN EN 12350-5) was achieved. This ensures an adjustment of the air void content from 1.0 to 2.0% by volume (DIN EN 12350-7).

All samples were demoulded after 2 days, the open samples were stored for a further 12 days at 100% relative humidity and 20°C and then in a climate of 20/65; half were packed in aluminium-laminated PE foil after 2 days and stored at 20°C. The compressive strength was determined on cylinders of 150 mm diameter and 300 mm height.

Analogous to DIN 52450, discontinuous measurements were carried out on prisms with dimensions of 75 mm x 75 mm x 280 mm using measuring instrument B for length changes (Fig. 2).



Fig. 2: Measuring instrument with dial gauge from Schleibinger - left with open prism
- right packed with aluminium-laminated PE-foil

3. RESULTS AND DISCUSSION

3.1 FRESH CONCRETE

The back-stiffening of the concretes with SAP led to increased use of superplasticizers, which in turn led to heavy bleeding, but interestingly not to sedimentation. The result is water on the surface and between the aggregate and the cement matrix. As the effect is against gravity, the separating layers are horizontal, resulting in anisotropic concrete. By using a stabilizer in low concentration, it was possible to prevent sedimentation. The addition of SAP including an increased amount of superplasticizer led to a strong delay of the concretes. These concretes could only be demoulded after 2 days.

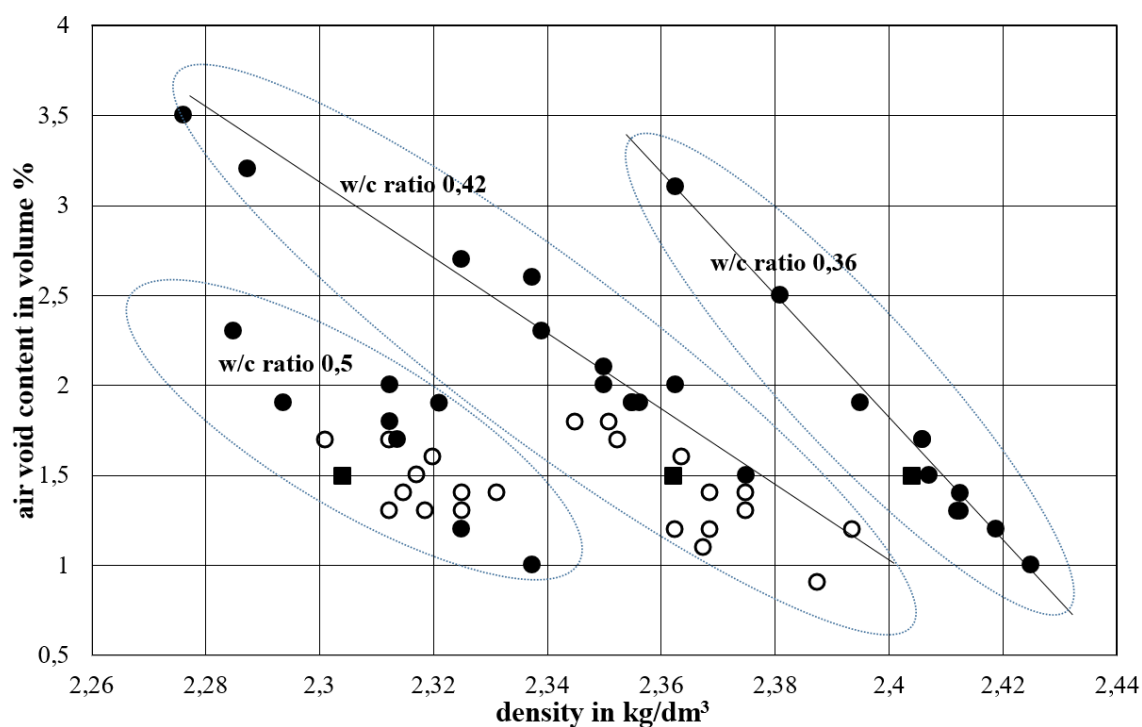


Fig. 3: Correlation air void content vs density of fresh concrete;
 • reference; ■ calculated; ° concrete with SAP

Of all fresh concretes, density and the air void content were determined. If the fresh concrete density is plotted against the air void content (Fig. 3), three families can be identified, as there are only three basic formulations. The following things are also noticeable:

- a. There is a relationship between air void content and density.
- b. The theoretical density of the concretes is lower than the measured density. Already at the beginning of the water addition the alkali and partly calcium,

compounds dissolve and thus increase the density in the mixing water - the density of the concrete increases.

- c. The concretes with SAP have a lower density than the reference concretes. This indicates a selective absorption of water in the SAP's. The alkalis and above all the alkaline earths can only be partially absorbed into the super absorbers.

3.2 HARDENED CONCRETE

3.2.1 Compressive strength

Only when pressing the concrete cylinders containing SAP a very strong ammonia odour was noticeable, which changes into an ethanolamine odour after a few seconds. This is a clear indication of the degradation of the organic polymers.

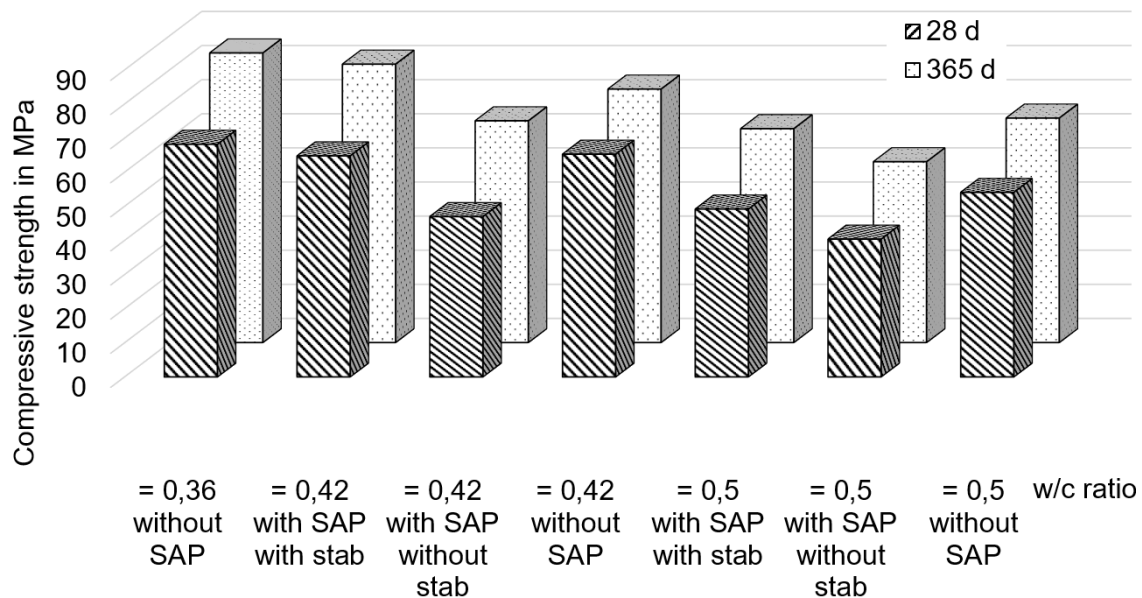


Fig. 4: Compressive strength of open cylinders (150 x 300 mm)

If you look at Fig. 4 and 5, you can draw the following conclusions:

- The differences in strength between the packed and unpacked cylinders after 365 days are only slight.
- The lower the w/c ratio, the higher the strength.
- Cylinders with SAP but without stabilizer show all reduced strengths due to their weakened structure between aggregate and cement matrix.
- The differences in strength between cylinders without SAP and cylinders with SAP and stabilizer with the same w/c ratio are very small.

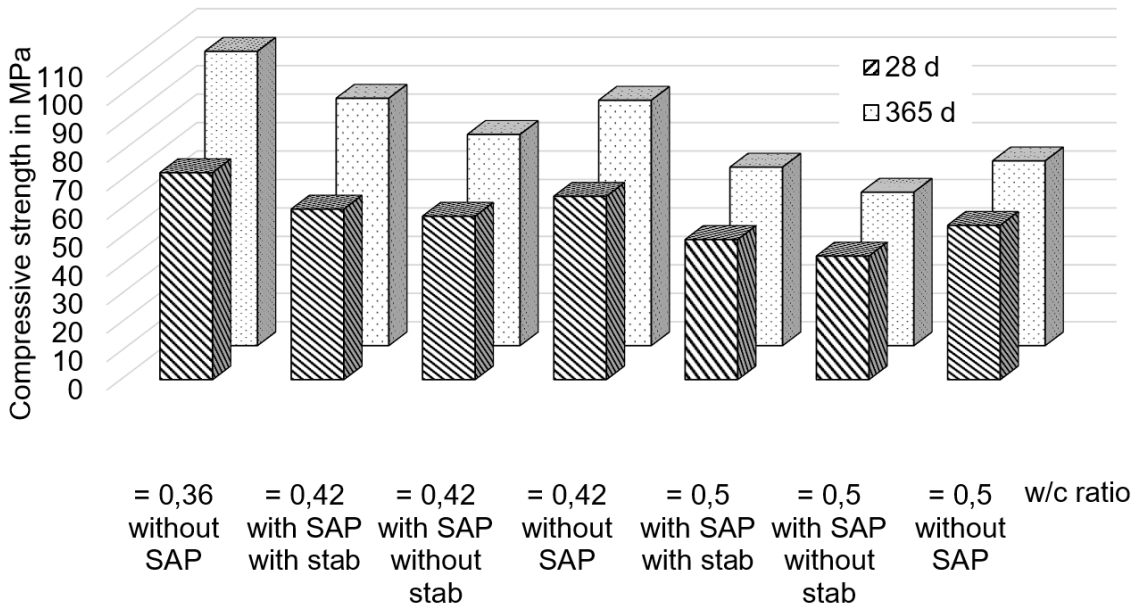


Fig. 5: Compressive strength of cylinders wrapped in alumina-laminated folio

3.2.2 One-dimensional deformation behaviour

The weight loss of the open prisms was measured over 460 days (Fig. 6).

In summary, the following results are interesting:

- The lower the w/c ratio, the lower the weight loss.
- With the same w/c ratio value, the SAP modified concretes have higher water losses than the non-modified concretes.
- SAP modified concretes with stabilizer lose less water than concretes without stabilizer.

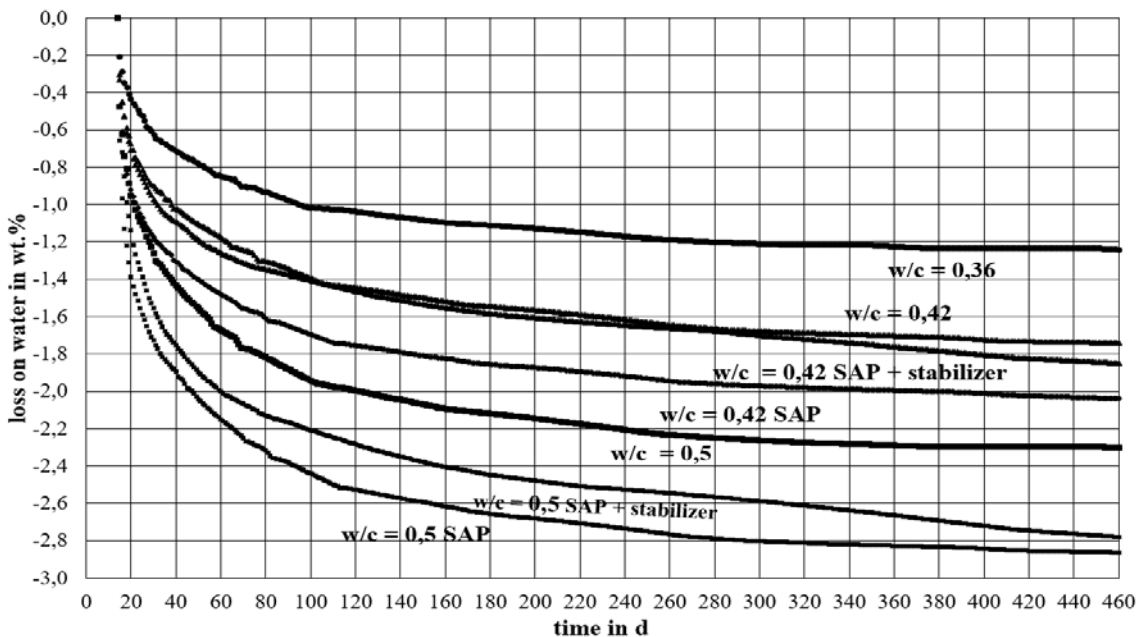


Fig. 6: Loss on drying over time (open prism 75 x 75 x 280 mm³)

These results are in good agreement with the theory in the introduction. If the SAP influences the chemical composition of the hydrate phases in such a way that less water is incorporated into the structure by the degradation products, such as ethanolamine, occupying the lattice sites of the water molecules, more water evaporates via the capillaries.

In concretes with SAP but without stabilizer, the water evaporated faster due to the weakened sedimentation layers between the aggregate and the cement matrix.

The greatest effect of shrinkage independent of the w/c ratio and the additives is the loss of water through drying (called drying shrinkage) (Fig. 7). While the packed prisms shrink by a maximum of 0.25 mm/m after 560 days (autogenous shrinkage), the shrinkage of the open prisms is up to 0.8 mm/m.

Looking at the shrinkage process (Fig. 7) of the single concretes, the following results are obtained:

- a. The SAP-modified concrete shrinks less because the chemical degradation of SAP's provides water for post-hydration on the one hand and the degradation products are incorporated into the hydrate phases on the other.

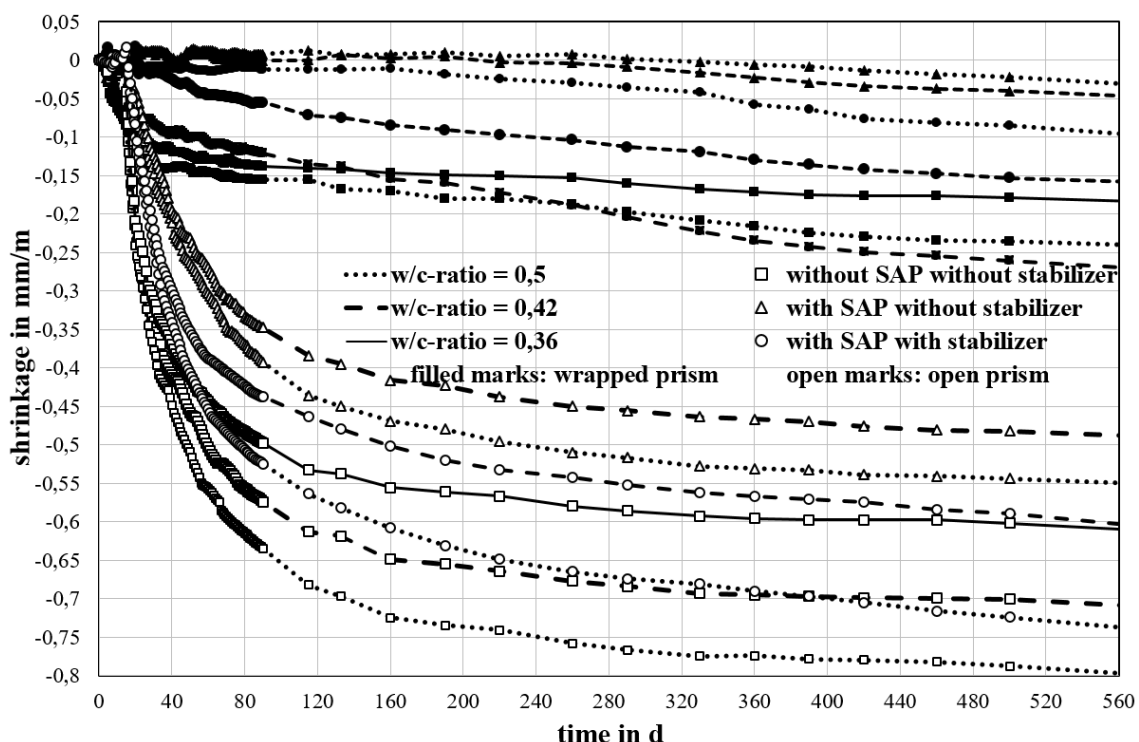


Fig. 7: Shrinkage of concrete prisms (75 x 75 x 280 mm) over 560 d

- b. If more water is available (high w/c ratio), the concrete (without SAP) normally shrinks more. Already Graf [6] described 70 years ago this effect in detail. In those days, e.g. superplasticizers based on polycarboxylate ethers,

did not exist. Therefore, concretes with w/c ratios below 0.4 were not in focus. However, this behaviour of increased shrinkage at elevated water contents does not always apply. Investigations [6, 7] show that concretes, which cannot lose any or very little water, pass through a shrinkage minimum when the w/c ratio changes. Concretes with both high and low w/c ratios shrink more than concrete with an average w/c ratio (Fig. 7; packed prisms without SAP up to approx. 140 days).

- c. The SAP concretes modified with stabilizers do not exhibit water secretion. These concretes therefore have a higher effective w/c ratio and shrink more than the unmodified ones.

4. SUMMARY

At the beginning of the hydration of cement clinker phases, amorphous to microcrystalline phases are formed which are difficult to access analytically. If hydration continues, the crystalline areas grow at the expense of the amorphous ones. The presence of organic molecules such as shrinkage reducers, super-plasticisers or air-entraining agents changes the crystallization process. By adsorption on preferred surfaces, the integration into the crystal lattice takes place. This has serious consequences:

1. If organic molecules occupy hydrate water layers, a reduced shrinkage is observed.
2. The morphology of the crystals can change dramatically. On the one hand, the size but also the length to thickness ratio can change.
3. The growing together of the single crystals influences also the strengths. The question arises: Which molecular structures do the contact points have?

Thus, many effects play a role in the volume change of cementitious building materials. Since the result of the hydration of the clinker phases does not correspond to an exact stoichiometric composition, the following influences play a role:

- a. The composition and the ratio of the main element oxides Ca, Si, Al, Fe,
- b. The content of alkalis, Mg^{2+} , Ti^{4+} , SO_4^{2-} , Cl^- , influences the lattice spacing due to the incorporation into the crystals. Furthermore, Na^+ and K^+ increase the pH value.

- c. The addition of organic, polar chemicals such as shrinkage reducers, superplasticisers, air-entraining agents, etc. also have a major influence on shrinkage.
- d. The temperature during the entire hydration process: high temperatures favour lower hydrate levels [7].
- e. Water: at the beginning of hydration as w/c ratio, through evaporation as water loss and through diffusion from outside (Fig. 8). In hardened concrete, only rearrangements and reactions with water take place. In this processes calcium silicate hydrates release water. This water can then react with non-hydrated clinker phases or evaporate via the concrete surface.

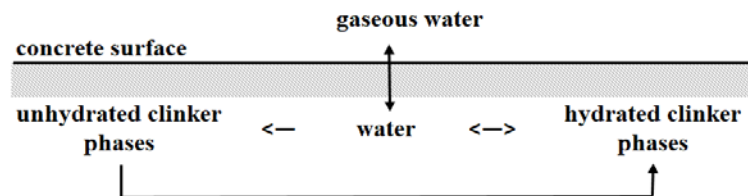


Fig. 8: Schematic sequence of cement hydration

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