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Carboxylates and sulfates of polysaccharides for controlled internal water release during cement hydration

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ABSTRACT

Calcium and aluminium carboxylates and sulfates of polysaccharides form hydrogels. Four Al- and three Ca-salt hydrogels of such polysaccharides, which were found to be stable enough to be mixed into fresh Portland cement pastes of low initial water-to-cement ratio of 0.275, were compared with respect to their water retardation potential using non-destructively operating low-field ^{1}H NMR relaxometry. All of the investigated hydrogels release their water to the cement mainly during the accelerated period of cement hydration. At a degree of hydration of about 0.7 the water in the hydrogels is consumed completely by the hydration reactions. Based on Powers' hydration model the development of the volumetric phase distribution of the investigated hydrating cement with internal curing by the hydrogels was quantified. Within the hardening cement the Ca-salt hydrogels are more stable than the Al-hydrogels which is concluded from the changes of the T_2 relaxation times during the cement hydration.

1. Introduction

Internal concrete curing as alternative solution to traditional external curing methods becomes more and more important, especially for concrete of low water-to-cement (*w*/*c*) ratios. Internal curing is achieved by addition of water containing or water absorbing additives to fresh cements or concretes prior to their casting. The additives with temporary delayed release of water deliver water to the hardening cement matrix during the hydration process. This curing method promotes a homogenous curing of the cement matrix which allows a continuous cement hydration. Jensen and Hansen [1] interpret the effectiveness of internal curing by addition of water containing superabsorbant polymers (SAP) where, in a water entrained cement paste the degree of hydration is increased and, from the point of view of pore size distribution, the water entrained cement paste offers a very dense pore structure between the macropores predesigned by the SAP particles [1]. It is noticed that the almost spherically predesigned macropores reduce the strength less than the same volume of fine pores of uncontrolled shape [2].

For concrete with internal curing an increased relative humidity is often discussed [1,3–7] which is assumed to decrease the self-desiccation [4,8,9]. A reduced tendency of forming of microcracks in high performance concrete (HPC) [3,5,7], a reduced autogenous shrinkage [1,3,6,7,9,10–18] and drying shrinkage [7] as well as in some cases improved mechanical properties and an improved durability [6,16,19,20] of concrete compared to reference samples without internal curing were reported.

As materials for internal curing of high performance concretes water-saturated lightweight aggregates (LWA) are commonly used (e.g., [3,8,10,21–26]). Other intelligent materials are the already mentioned superabsorbent polymers, which absorb water directly after addition of mix water to the mixture and release it later to the hardening cement. Due to these promising results, SAPs (e.g., [1,11,19,27,28]) are increasingly investigated for the use for internal curing of concretes of low *w*/*c*-ratios. One of the first examples for application in practice is described in [28]. In our own previous work [29], where we realized internal curing of a white Portland cement by addition of Ca-alginate, a water-saturated polysaccharide hydrogel, the transition of the curing water from the hydrogel into the hydrating cement matrix was monitored non-destructively in dependence on the hydration time using low-field ^{1}H NMR relaxometry.

Based on these investigations additional hydrogels of polysaccharide carboxylates and sulfates were examined for internal curing applications. Especially the polysaccharide salts of bi- and trivalent metal ions seem to be promising, since they form stable three-dimensional networks via hydrogen bridges and via the bi- and trivalent metal ions of the carboxylate and sulfate groups, respectively. In the present study we focused on the hydrogels of calcium- and aluminium-salts of alginic acid, gellan and carboxymethyl cellulose (CMC) which belong to the group of carboxylates as well as on Ca- and Al-salts of carrageen (sulfates).

Using low-field ^{1}H NMR relaxometry, we compare the carboxylates and sulfates of the polysaccharide gels, which differ

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concerning the chemical structure, the functional groups and the metal ions, with respect to their water retardation potential and to their stability in hydrating cements and we investigate the water dynamics during internal curing. The methodology of low-field ^1H NMR relaxometry was introduced and extensively described in [29,30]. It is quick and allows us to follow the hydration progress and water transition non-destructively on one sample with a time-resolution of a few minutes. Finally, based on the NMR results, the volumetric distribution of phases during hydration with internal curing is quantified using the Powers' model [31].

2. Materials and methods

2.1. Polysaccharides and their salts

The polysaccharides alginate, gellan, carrageenan and CMC belong to the group of biopolymers. Alginate is the salt of alginic acid. It is a linear copolymer with homopolymeric blocks of (1–4)-linked β-D-mannuronate and its C-5 epimer α-L-guluronate, covalently linked together in different sequences or blocks, (see e.g. [32]).

Gellan consists of D-glucose, D-glucuronic acid and D-rhamnose in a ratio of 2:1:1, in which about half of the monomers are acetylated [32]. The structure of carrageenan is based on repeating D-galactose-4-sulfate and 3,6-anhydro-D-galactose linked α-(1–4) and β-(1–3), respectively [32].

These polysaccharides and their salts, respectively, are commonly used as thickeners in food and pharmaceutical products. In some extent they are contained for instance in dental products, detergents and water-based paints. Na-CMC was used in cementitous materials to improve the durability and to prevent its deterioration [33,34]. Furthermore water-soluble polysaccharide derivatives like CMC are applicable as dispersants for mineral binders [35]. Biopolymers, for instance alginate, are described as alkali-free liquid setting and hardening accelerator for cements and mortars [36]. Furthermore, alginate and also CMC products are utilized in calcium phosphate cements for implanting of prostheses (bones, tooth), where they improve the setting behaviour, the consistency and the mechanical properties of these biocements [37,38]. With the exception of the Ca-alginate hydrogel these biopolymers are not yet investigated with respect to their water retardation properties in internal curing application of cementitious materials.

2.2. Preparation of polysaccharide hydrogels

The hydrogels of the Ca- and Al-salts of alginic acid, gellan, carrageen and carboxymethyl cellulose were prepared from the commercially available sodium salts of the polysaccharides. Sodium alginate (Manugel DJX), carrageenan (GENUGEL type Cl-125, a mixture of Ca-carrageenan and sodium chloride) and low-acyl sodium gellan gum (KELCOGEL AFT) were obtained from CP Kelco (Germany) and sodium carboxymethyl cellulose from Wolff Cellulosics GmbH & Co.KG (Germany).

Prior to mixing with the cement pastes, the sodium salts of polysaccharides were transformed into the Ca- and Al-salts by ion exchange reaction [39,40]. Following the well established preparation of Ca-alginate from sodium alginate and calcium chloride [39], the aqueous solution of the sodium polysaccharides (1%) were added drop by drop to a 1 molar calcium chloride and aluminium acetate solution, respectively, yielding spheres of the hydrogels of diameter of about 2 mm. In case of Ca- and Al-gellan and of Al-carrageenan the polysaccharide solutions were heated to 50 °C and were dropped to the chloride and acetate solutions, respectively. The obtained hydrogels were stored in air-proof containers, where they are stable over long periods of time (at least months).

For the preparation of the Ca-carrageenan hydrogel 1.6 g GENUGEL® type Cl-125 was dissolved in 50 ml water at a temperature of about 85 °C. When the solution is cooled to room temperature a firm gel is formed [40]. For introduction into the cement lime, the hydrogel was cut to small pieces of about 4 mm^3. All Ca- and Al-hydrogels offer a sufficient mechanical gel stability to be mixed into fresh cement pastes and are resistant to pH-values of 12–13.

2.3. Cement paste preparation

All cement paste samples were prepared using an ordinary Portland cement (CEM I 42.5 R). Sample R is the reference sample without addition of hydrogels for internal curing. For the studies of hydration with internal curing the hydrogels were added to the freshly mixed cement pastes, prepared with an initial w/c-ratio of 0.275. The amount of hydrogels added was chosen in such a way that the total w/c-ratio of the samples increases from 0.275 to 0.3 in each case. The samples were carefully mixed to achieve a homogeneous distribution of the hydrogels. They were introduced into NMR sample tubes (outer diameter: 20 mm, filling level: 30 mm) which were sealed by a cap to prevent the evaporation of water.

Two further samples were prepared with superplasticizer (sp) to achieve a reasonable workability (samples 4c and 4d). As superplasticizer, a polycarboxylate ether was utilized, which was dosed to the mix water prior addition of cement. All investigated samples are listed in Table 1.

2.4. Low-field NMR relaxometry

The dynamics of water and the changes of transverse relaxation time T_2 were continuously monitored by low-field NMR relaxometry during the first 24 h, in case of samples with superplasticizer during the first 48 h of hydration. The methodology and equipment of the measurements including the transformation of data into the T_2-relaxation time distributions $p(T_2)$ are described in detail in Refs. [29,30]. A CPMG NMR pulse sequence with an echo spacing of 100 μs and a number of spin echos of 2048 was used (repetition delay time: 5 s, number of scans: 64, time for one measurement: about 5 min). This setting allows a simultaneous observation of T_2-relaxation time of the water in the cement phase as well as in the hydrogels. The obtained magnetization curves were analyzed using commercial inverse Laplace transformation software yielding the T_2-relaxation time distributions. The hydration progress and the transition of water were followed with a time-resolution of a few minutes. The measurements were performed at room temperature (about 20 °C).

3. Results and discussion

Fig. 1a plots the T_2-relaxation time distributions of the reference sample (sample R) detected after 1, 8, 16 and 24 h of hydration time. Only one peak for the physically bound water which belongs to the hydrating cement is observed. Its maximum shifts from about 4.5 ms at the beginning of the hydration to T_2-relaxation times of less than 1 ms during the observation period of 24 h. Furthermore a decreasing area under this peak is observed. Since the low-field NMR technique only allows one to observe the physically (gel and capillary) bound water, the reduced peak area is caused by the water consumption of the hydration reactions.

Fig. 1b shows the time-dependence of the T_2-relaxation time distribution for the cement paste with addition of Al-alginate as internal water source (sample 2b) as a typical example for samples with internal curing by hydrogels. These distributions show always an intensive peak at $T_2 < 10$ ms, which shows the same behaviour as observed in the reference sample. It is attributed to the physically

Table 1
Samples prepared for NMR studies of water transition during internal curing by Ca- and Al-hydrogels. The table lists the sample ID, the added water containing hydrogels and the content of superplasticizer (sp) referred to the content of cement. Additionally, the T_2-relaxation times of the pure hydrogels (column 4) and the T_2-relaxation times of the hydrogels inside of hydrating cement determined directly after sample preparation (column 5) are listed.

Sample	Hydrogels	sp/%	T_2/ms of hydrogel	T_2/ms of hydrogel inside of cement
R	–	–	–	–
1	Al-CMC	–	240	240
2a	Ca-alginate	–	130	130
2b	Al-alginate	–	80	80
3a	Ca-carrageenan	–	400	400 (720[a])
3b	Al-carrageenan	–	170	170 (380[a])
4a	Ca-gellan	–	380	290
4b	Al-gellan	–	330	300
4c	Ca-gellan	0.275	380	380
4d	Al-gellan	0.275	330	300

[a] Increase of T_2-relaxation time during the first hour of hydration time.

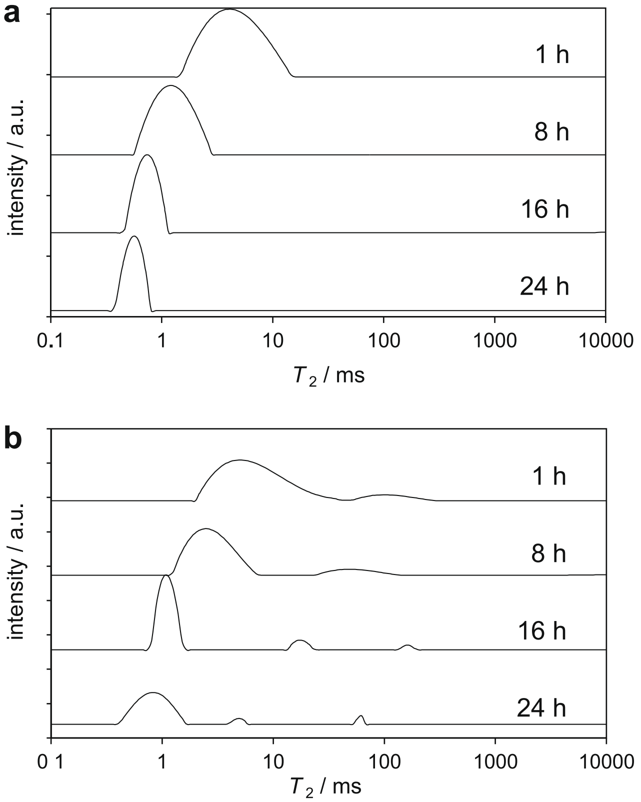

Fig. 1. Transverse relaxation time distributions $p(T_2)$: (a) during cement hydration of reference sample (sample R) and (b) during cement hydration with internal curing by Al-alginate (sample 2b).

bound water in the cement phase. The smaller peak observed at longer relaxation times (in case of the selected sample (sample 2b, Fig. 1b) at 80 ms, detected after 1 h) is assigned to the water trapped in the hydrogel since its T_2-relaxation time (position of the peak maximum) corresponds well with the T_2-value of the pure water-saturated Al-alginate (see Table 1).

For all samples the comparison between independent T_2-measurements of the water-saturated hydrogels and their T_2-values detected inside the hydrating cement directly after sample preparation is listed in Table 1 (columns 4 and 5). Generally, these values agree very well with each other, which supports the above discussed assignment of the peaks in the T_2-relaxation time distributions. Only for the samples prepared with Ca- and Al-carrageenan (samples 3a and 3b), the peak maxima of the hydrogel water shift to significantly higher T_2-values during the first hour of the observation period (see Fig. 2a, sample 3b and Table 1). We interpret this initial increase of T_2 by a decomposition of the hydrogel structure inside the hydrating cement. Ca- and Al-carrageenan hydrogels offered a decreased gel strength in extended time tests of pH-resistance as also described in [41]. Nevertheless, despite the observed decreased gel stability, the water remains inside of the predesigned macropores of the hydrogel until it is consumed by the hydration reactions (see Fig. 2a, sample 3b for $t_n > 1$ h).

In the case of samples with internal curing by all Al-salt hydrogels a split of the intensities characteristic for the hydrogel water is generally observed after about 10 h (e.g., Figs. 1b and 2a). In case of the Al-alginate (Fig. 1b) the position of the maxima of the two peaks is about 20 ms and about 130 ms. The T_2-relaxation time of 130 ms is in accordance with the T_2 of Ca-alginate, compare Table 1. Consequently, it can be assumed that the Al-cations from the hydrogel are partially exchanged by Ca-cations from the cement phase. The subsequent shift of both peak maxima to smaller T_2-values can also be

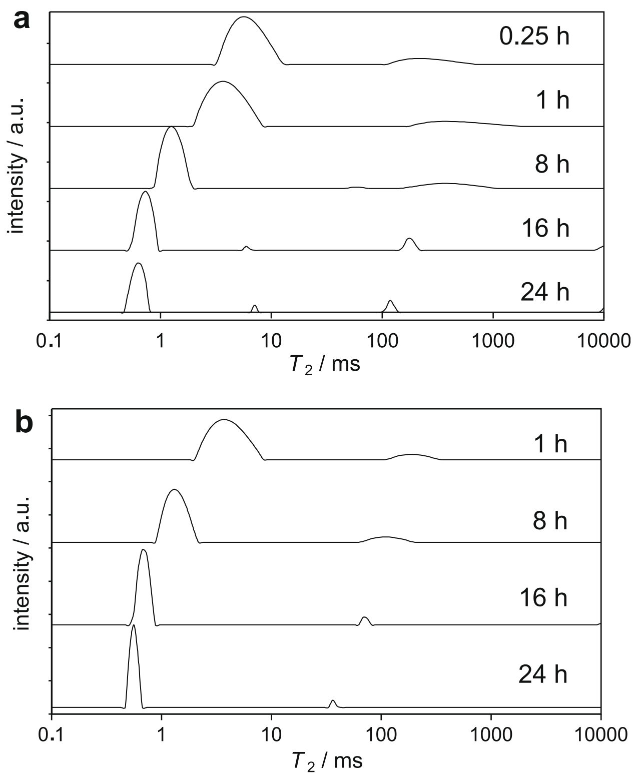

Fig. 2. Transverse relaxation time distributions $p(T_2)$ of hydrating cement with internal curing by (a) the hydrogel Al-carrageenan (sample 3b) and (b) Ca-gellan (sample 4a).

interpreted by a diffusion of paramagnetic Fe^{3+} ions from the cement (content of Fe_2O_3 in the ordinary Portland cement about 3% by weight) into the water of the gels which are known to enhance the relaxation rate and thus lead to shorter T_2-relaxation times [30,42]. From these observations we conclude that the stability of the Al-hydrogels inside the hydrating cement is lower than that of the Ca-hydrogels.

As an example for the samples prepared with Ca-hydrogels, the T_2-distributions of the cement paste prepared with addition of Ca-gellan are presented (sample 4a, Fig. 2b). During hydration, the T_2-peak of the Ca-gellan hydrogel does not split but loses intensity due to the water consumption of the hydration reaction and shifts slightly to shorter relaxation times, which we interpret as result diffusion of Fe^{3+} ions from the cement paste into the hydrogel.

In all samples prepared with addition of hydrogels, the intensity of the gel peaks decreases during the hydration process which indicates the migration of the water from the hydrogels into the hydrating cement matrix (see examples presented in Figs. 1b, 2a, 2b). From the analysis of the relaxation time distributions the time-dependence of the content of physically bound water in the cement phase and of water trapped inside the hydrogels is obtained. As an example, Fig. 3 shows the time-dependence of the physically bound water in the cement phase, in the hydrogel and the sum of both for the sample with Ca-gellan hydrogel without and with superplasticizer (samples 4a and 4c). In case of sample 4a (without superplasticizer), the physically bound water in the cement phase as well as inside of the hydrogel remains constant up to about two hours after cement paste preparation which means that no water is consumed. This coincides with the so called dormant period [43]. With the onset of the accelerated period, which is the period of the highest rate of hydration reaction [43], the observed water content starts to decrease. After 25 h, about 50% of the physically bound water in the hydrating cement is consumed (graph of sample 4a in Fig. 3). This water is consumed by the formation of solid hydration products like calcium silicate hydrate, portlandite and ettringite [43] and thus does not contribute anymore to the observed low-field NMR signal. During this period, a significant transition of water from the hydrogels into the hydrating cement matrix is detected (sample 4a, Fig. 3). At the end of observation period no water is detectable in the Ca-gellan hydrogel. Consequently, this additional water has completely migrated from the hydrogel into the hydrating cement matrix.

Due to the retarding influence of the superplasticizer the onset of the accelerated period is delayed. This delay amounts to about 20 h in the investigated sample with superplasticizer (graphs of sample 4c in Fig. 3). After the extended dormant period, the observed water content decreases significantly during the accelerated period. The transition of the additional water in the hydrogel is also delayed by the dormant period prolonging influence of the superplasticizer (sample 4c, Fig. 3).

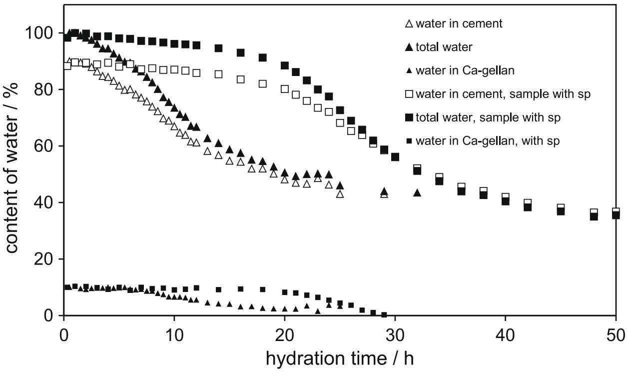

Fig. 3. Time-dependence of the amount of physically bound water in cement (empty symbols), of the curing water in the hydrogels (small full symbols) and the sum of both (big full symbols) for samples with internal curing by Ca-gellan, without (sample 4a, triangles) and with superplasticizer (sample 4c, squares). 100% refers to the initial total amount of water in the samples.

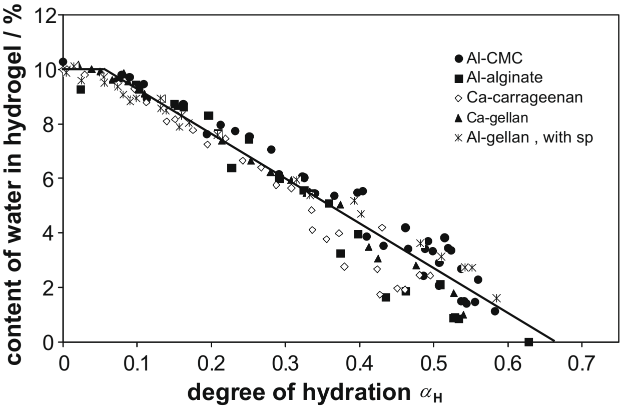

Fig. 4. The content of water in the hydrogels in dependence on the degree of hydration of cement for samples with internal curing by Al-CMC (sample 1), Al-alginate (sample 2b), Ca-carrageenan (sample 3a), by Ca-gellan (sample 4a) and by Al-gellan in presence of superplasticizer (sample 4d). Ten percentage refers to the relative amount of water, detected inside of the hydrogel directly after sample preparation.

In Fig. 4 the content of water trapped in the hydrogels is plotted as a function of the degree of hydration for five samples with hydrogels. The degree of hydration α_H at time of hydration t is calculated from the total NMR signal intensities M_0 and $M(t)$, which mean the initial content of physically bound water (M_0) and the corresponding amount at time t, respectively, by the relation:

$$\alpha_H = \frac{m_{w,t}}{m_{w,\max}} = \frac{w/c_{0,ic}}{0.3} \cdot \frac{(M_0 - M(t))}{M_0} \tag{1}$$

Here $m_{w,t}$ denotes the content of chemically bound water at hydration time t and $m_{w,max}$ is the theoretical chemically bound water in case of completed hydration [44]. It can be calculated from the stoichiometric bound water of the clinker phases of the CEM I. By utilizing utilized by the relations in [44] 1 g of the cement binds about 0.3 g of water chemically which is in good agreement with own gravimetric measurements.

Since at hydration time t, the NMR signal intensity $M(t)$ is proportional to the sum of the capillary water and of the water bound in the gel pores, the amount of water, chemically bound at that time, $m_{w,t}$, can be calculated by the difference between the initial NMR signal M_0 and the signal intensity $M(t)$ detected at the hydration time t. The initial water-to-cement ratio in the sample is composed of the mix water in the sample and of the additional curing water: $w/c_{0,ic} = 0.275 + 0.025 = 0.3$.

The presentations of the water trapped in the hydrogels as function of the degree of hydration reflect a similar water retention for all hydrogels. In Fig. 4 it is presented for the samples with internal curing by Al-CMC (sample 1), Al-alginate (sample 2b), Ca-carrageenan (sample 3a), Ca-gellan (sample 4a), and by Al-gellan in presence of superplasticizer (sample 4d). The main transition starts after the degree of hydration is increased to about 0.1. At a degree of hydration of 0.5, the water content in the additive dropped to (3 ± 1)%, which means that roughly 2/3 of the initial curing water migrated from the hydrogels into the hydrating cement. At degrees of hydration of about 0.6, which according to Fig. 4 correspond to roughly 1/10 of the initial curing water content (or 1% of the total initial water content in the samples), the sensitivity of the applied NMR method reaches its limits for a further quantification of the water content in the hydrogels. Nevertheless, the NMR measurements clearly show that at least 9/10 of the initial curing water was consumed at a degree of hydration of 0.6 and higher. Thus, the curing water is almost completely consumed by the hydration reaction (Fig. 4).

Using these results of NMR relaxometry measurements the volumetric phase distributions of the solid hydration products and of the unhydrated cement as well as the volume fractions of water in gel and capillary pores calculated by the relations given in [1] are summarised for hydrating cement with internal curing by the hydrogels in the schematically presentation according to Powers' hydration model (Fig. 5) [1,31].

It is known that at initial *w/c*-ratios lower than 0.42, additional free access water will increase the degree of hydration [1]. That means that the maximum degree of hydration of 0.66 for the cement paste of initial w/c_0 of 0.275 (as in the investigated samples) will be increased in our experiments by internal curing using the hydrogels ($w/c_{0,ic} = 0.275 + 0.025$) to 0.72 (see Fig. 5). However, the initial porosity of the hydrating cement is in accordance with a cement of w/c_0 of 0.275, while geometrically predesigned macropores are added by the hydrogels. The hydrated cement between these macropores will have the properties of a cement of $w/c_0 = 0.275$ with optimum curing conditions. It is also shown that the fraction of gas-filled micropores is reduced by internal curing (Fig. 5). Consequently, it can be expected that also the chemical shrinkage, which may be calculated using the relations in [1], will be decreased. For example, measurements on an ultra high performance concrete with internal curing by the hydrogel Ca-alginate of $w/c_{0,ic} = 0.282 + 0.022$ showed nearly the same extent of shrinkage like the reference concrete of w/c_0 of 0.282 [45].

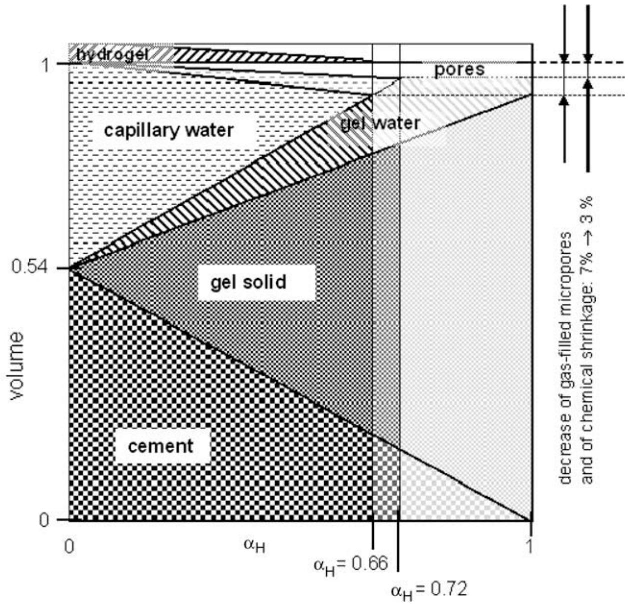

Fig. 5. Volumetric phase distribution in dependence on the degree of hydration α of hydrating cement with internal curing by hydrogel, $w/c_0 = 0.275 + 0.025$. It is shown that α_H is increased and the extent of chemical shrinkage can be reduced by internal curing.

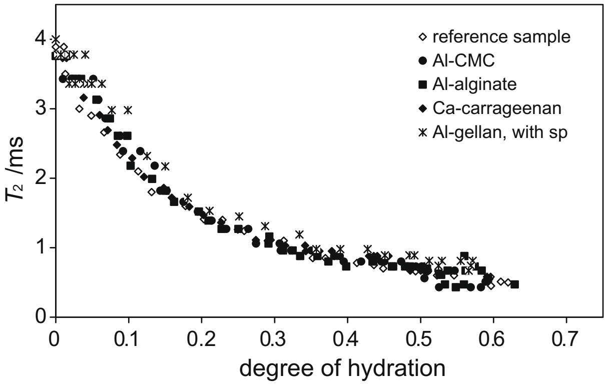

Fig. 6. Dependence of the logarithmic mean transverse relaxation time $\langle T_2 \rangle$ of physically bound water in hydrating cement of reference sample R and of samples with internal curing by Al-CMC (sample 1), Al-alginate (sample 2b), Ca-carrageenan (sample 3a) and by Al-gellan in presence of superplasticizer (sample 4d) on the degree of hydration.

Fig. 6 plots the logarithmic mean transverse relaxation times $\langle T_2 \rangle$ of the physically bound water in the hydrating cement paste in dependence on degree of hydration. Generally, the T_2-values decrease with increasing degree of hydration indicating a decreasing pore size of the micropores. Since there is no significant difference in the development of the logarithmic mean $\langle T_2 \rangle$ values between all samples including the reference sample, it can be concluded that internal curing by addition of the suggested Ca- and Al-hydrogels has no negative influence on the development of micropore structure of the cement matrix.

4. Conclusions

Seven different hydrogels obtained from calcium and aluminium-salts of polysaccharides were investigated for their suitability for internal curing of a hydrating ordinary Portland cement using non-destructively operating low-field ^{1}H NMR relaxometry. From this study the following conclusions can be drawn:

- While the polysaccharides differ with respect to the chemical structure, the functional groups as well as the cations, which stabilise the gel structure, their hydrogels deliver the water to the hydrating cement matrix mainly during the accelerated period of cement hydration. It was found that the transition of water starts after the degree of hydration is increased to about 0.1. At degree of hydration of about 0.6, the curing water has almost completely migrated from the hydrogels into the hydrating cement matrix.
- In case of addition of superplasticizer the transition is temporally delayed by its retarding influence on the hydration process, but the main transition of water occurs also during the accelerated period starting with some delay and follows the same path as for the cement hydration without superplasticizer, if analyzed as function of the degree of hydration.
- Based on Powers model the volume fractions of water inside the hydrogel, of the capillary bound water, of water in gel pores, of the solid hydration products and of the unhydrated cement were calculated for the investigated samples. It could be shown that by the addition of the hydrogels (increase of initial $w/c_0 = 0.275$ by 0.025) the maximum of the degree of hydration is increased and the development of gas-filled micropores and consequently the extent of chemical shrinkage can be reduced.
- Additionally, it is confirmed from the dependence of mean T_2 relaxation time on the degree of hydration that the internal curing with such hydrogels does not significantly influence the micropore structure of the cement matrix (excluded the macropores predesigned by the hydrogels) of the investigated samples.
- From changes of the T_2 relaxation times it was concluded that, inside the hydrating cement, the calcium salt hydrogels are more stable than the corresponding aluminium hydrogels.
- The hydrogels of gellan were found to be most suitable for internal water curing during the accelerated period of cement hydration, because they offered the best mechanical stability and resistance to high pH-values compared to the other hydrogels.

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References

[1] Jensen OM, Hansen PF. Water entrained cement-based materials, part I, principle and theoretical background. Cem Concr Res 2001;31(4):647–54; Jensen OM, Hansen PF. Water entrained cement-based materials, part II, experimental observations. Cem Concr Res 2002;32:973–8.

[2] Popovics S. Strength and related properties of concrete. New York: John Wiley & Sons; 1998. p. 309–11 and 373–5.

[3] Reinhardt HW, Weber S. Hochfester Beton ohne Nachbehandlungsbedarf. Beton und Stahlbeton 1997;92(2):37–41. and 92(3):79–83.

[4] Lura P, Jensen OM, Igarashi SI. Experimental observation of internal water curing of concrete. Mater Struct 2007;40(2):211–20.

[5] Zhutovsky S, Kovler K, Bentur A. Influence of cement matrix paste properties on the autogenous curing of high performance concretes. Cem Concr Compos 2004;26(5):499–507.

[6] Wang F, Zhou Y, Liu Z, Hu S. Internal relative humidity and autogenous shrinkage of low water/binder ratio concrete. In: Jensen OM, Lura P, Kovler K, editors. Volume changes of hardening concrete: testing and mitigation. Proceedings of the international RILEM conference, Denmark, August 2006. p. 51–6.

[7] Lura P, Durand F, Jensen OM. Autogenous strain of cement pastes with superabsorbent polymers. In: Jensen OM, Lura P, Kovler K, editors. Volume changes of hardening concrete: testing and mitigation. Proceedings of the international RILEM conference, Denmark, August 2006. p. 57–65.

[8] Akcay B, Tasdemir MA. Influence of lightweight aggregates on internal curing and fracture of concrete. In: Jensen OM, Lura P, Kovler K, editors. Volume changes of hardening concrete: testing and mitigation. Proceedings of the international RILEM conference, Denmark, August 2006. p. 31–40.

[9] Bentz DP, Jensen OM. Mitigation strategies for autogenous shrinkage cracking. Cem Concr Compos 2004;26(6):677–85.

[10] Geiker MR, Bentz DP, Jensen OM. Mitigating autogenous shrinkage by internal curing reprinted from high-performance structural lightweight concrete. In: John P, Ries, Thomas A. Holm, editors. ACI SP 218-9; 2004. p. 143–8.

[11] Igarashi S, Watanabe A. Experimental study on prevention of autogenous deformation by internal curing using superabsorbent polymer particles. In: Jensen OM, Lura P, Kovler K, editors. Volume changes of hardening concrete: testing and mitigation. Proceedings of the international RILEM conference, Denmark, August 2006. p. 77–86.

[12] Bentur A, Igarashi S, Kovler K. Prevention of autogenous shrinkage in high-strength concrete by internal curing using wet lightweight aggregates. Cem Concr Res 2001;31(11):1587–91.

[13] Zhutovsky S, Kovler K, Bentur A. Efficiency of lightweight aggregates for internal curing of high strength concrete to eliminate autogenous shrinkage. Mater Struct 2002;35:97–101.

[14] Kovler K, Bentur A. Efficiency of internal curing with water-saturated lightweight aggregates in terms of autogenous shrinkage reduction. In: Jensen OM, Lura P, Kovler K, editors. Volume changes of hardening concrete: testing and mitigation. Proceedings of the international RILEM conference, Denmark, August 2006. p. 107–16.

[15] Mönnig S, Reinhardt HW. Results of a comparative study of the shrinkage behaviour of concrete and mortar mixtures with different internal water sources. In: Jensen OM, Lura P, Kovler K, editors. Volume changes of hardening concrete: testing and mitigation. Proceedings of the international RILEM conference, Denmark, August 2006. p. 67–77.

[16] Lura P, Bentz DP, Lange DA, Kovler K, Bentur A. A pumice aggregates for internal water curing. In: Proceedings of the international RILEM symposium, Evanston, IL; 2004. p. 137–51.

[17] Craeye B, De Shutter G. Experimental evaluation of mitigation of autogenous shrinkage by means of a vertical dilatometer for concrete. In: Jensen OM, Lura P, Kovler K, editors. Volume changes of hardening concrete: testing and mitigation. Proceedings of the international RILEM conference, Denmark, August 2006. p. 21–30.

[18] Cusson D, Hoogeven TJ. Internal curing of high-performance concrete with pre-soaked lightweight aggregate sand for prevention of autogenous shrinkage cracking. Cem Concr Res 2008;38:757–65.

[19] Mönning S, Lura P. Superabsrobent polymers – an additive to increase the freeze–thaw resistance of high strength concrete. Adv Constr Mater 2007;5:351–8.

[20] Mechtcherine V, Schulze J, Dudziak L. Reducing of cracking potential of high-strength and ultra-high-strength concrete by internal curing. In: Beton+ Fertigteil-Technik, No. 2; 2007. p. 18–20.

[21] Kovler K, Souslikov A, Bentur A. Pre-soaked lightweight aggregates as additives for internal curing of high-strength concretes. Cem Concr Aggr 2004;26(2):131–8.

[22] Jóźwiak-Niedźwiedzka D. Scaling resistance of high performance concretes containing a small portion of pre-wetted lightweight fine aggregate. Cem Concr Compos 2004;27(6):709–15.

[23] Lura P, Bentz DP, Lange DA, Kovler K, Bentur A, van Bruegel K. Measurement of water transport from saturated Pumice aggregates to hardening cement paste. Mater Struct 2006;39:861–8.

[24] Bentz D, Hallek PM, Grader AS, Roberts JW. Four-dimensional X-ray microtomography study of water movement during internal curing. In: Jensen OM, Lura P, Kovler K, editors. Volume changes of hardening concrete: testing and mitigation. Proceedings of the international RILEM conference, Denmark, August 2006. p. 11–20.

[25] de Jesus Cano Barrita F, Bremner TW, Balcom BJ. Use of magnetic resonance imaging to study internal moist curing in concrete containing saturated lightweight aggregate. In: Ries JP, Holm TA, editors. ACI SP 218-9, Farmington Hills, MI; 2004. p. 143–8.

[26] Bentz DP, Snyder KA. Protected paste volume in concrete: extension to internal curing using saturated lightweight fine aggregate. Cem Concr Res 1999;29(11):1863–7.

[27] Lura P, Durand F, Loukili A, Kovler K, Jensen OM. Compressive strength of cement pastes and mortars with superabsorbent polymers. In: Jensen OM, Lura P, Kovler K, editors. Volume changes of hardening concrete: testing and mitigation. Proceedings of the international RILEM conference, Denmark, August 2006. p. 117–27.

[28] Mechtcherine V, Dudziak L, Schulze J, Steahr H. Internal curing by superabsorbant polymers (SAP) – effects on material properties of self-compacting fibre-reinforced high performance concrete. In: Jensen OM, Lura P, Kovler K, editors. Volume changes of hardening concrete: testing and mitigation. Proceedings of the international RILEM conference, Denmark, August 2006. p. 87–96.

[29] Friedemann K, Stallmach F, Kärger J. NMR diffusion and relaxation studies during cement hydration – a non-destructive approach for clarification of the mechanism of internal post-curing of cementious materials. Cem Concr Res 2006;36(5):817–26.

[30] Friedemann K, Schönfelder W, Stallmach F, Kärger J. NMR relaxometry during internal curing of Portland cements by lightweight aggregates. Mater Struct 2008. doi:10.1617/s11527-008-9355-0.

[31] Powers TC, Brownyard TL. Studies of the physical properties of hardened Portland cement paste. (nine parts) J Am Concr Inst 1946–1947;43:101–32, 249–336, 469–505, 549–602, 669–712, 845–80, 933–92.

[32] <http://www.foodnews.ch/x-plainmefood/20_lebensmittel.html>.

[33] Misha PC, Singh VK, Narang KK, Singh NK. Effect of carboxymethyl-cellulose on the properties of cement. Mater Sci Eng 2003;A 357:13–9.

[34] Lu Z, Zhou X. The waterproofing characteristics of polymer sodium carboxymethyl cellulose. Cem Concr Res 2000;30:227–31.

[35] Einfeldt L, Albrecht G, Kern A, Calado VM, Klemm D. Water-soluble polysaccharide derivatives used as dispersants for mineral binder suspensions, optionally contain hydroxyalkyl and/or sulfate groups. Degussa Construction Chemicals GmbH, 6 March 2002. DE Patent 10209812.

[36] Bösch K, Mai D. Alkali-free liquid setting and hardening accelerator for cement. European patent EP patent 0742179, 13 October 1999.

[37] Ishikawa K, Miyamoto Y, Kon M, Nagayama M, Asaoka K. Non-decay type fast-setting calcium phosphate cement: composite with sodium alginate. Biomaterials 1995;16(7):527–32.

[38] Dos Santos LA, De Oliveira LC, Rigo ECS, Carrodeguas RG, Boschi AO, De Arruda ACF. Influence of polymeric additives on the mechanical properties of α-tricalcium phosphate cement. Bone 1999;25(2):99–102.

[39] Nestle N, Galvosas P, Geier O, Vasenkov S, Kärger J. PFG NMR-diffusion studies in polysaccharide gels with and without innermagic field gradient. In: Proceedings of the 15th EENC, Leipzig, Germany; 2000.

[40] Multi-functional polysaccharide for gelling and texturizing. Product Information of Kelco (Monsanto Company); 1996.

[41] Urano T, Ina S. Admixture for cement or cement motar. JP patent 2002-298353, international Application No.: PCT/JP2003/004712, 14 April 2003.

[42] Bloembergen N, Purcel EM, Pound RV. Relaxation effects in nuclear magnetic resonance absorption. Phys Rev 1948;73:673–746.

[43] Stark J, Möser B, Eckart A. Neue Ansätze der Zementhydratation. ZKG International, Bauverlag; 2001.

[44] Stark J, Wicht B. Zement und Kalk. Hrsg. Bauhaus-Univ. Weimar, F.A. Finger-Institut für Baustoffkunde – FIB, Birkhäuser Verlag; 2000.

[45] Friedemann K, Stallmach F, Nestle N, Ma J, Tue NV, Kärger J. Hydratisierende Zemente mit innerer Nachbehandlung – Demonstration des Feuchteüberganges durch NMR Relaxationen – und Diffusionsuntersuchungen. In: Proceedings of the 16th ibausil, F.A. Finger-Institut für Baustoffkunde, J. Stark. Weimar, Germany, vol. 1; 2006. p. 367–74.