Influence of biopolymeric water-retaining admixtures on hydration of Portland cement studied using isothermal calorimetry

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Abstract. Viscosity enhancing and water-retaining admixtures based on the cellulose ethers are widely used in the building industry to improve the properties of concrete and ready-mix mortars. The study focuses on the influence of the alternative natural viscosity enhancing admixtures (sodium salt of alginic acid, carrageenan, diutan gum, xanthan gum, and hydroxypropyl derivatives of guar gum and chitosan) in doses of 0.1%, 0.5%, and 1% of the binder weight on the cement hydration. The study is carried out using isothermal calorimetry studying the heat flow and the total heat evolved during the reaction from the very beginning – the water-introduction into system. All of the studied biopolymers showed the set retarding ability as they are all of polysaccharidic origin. The dosage-dependency was significant for the hydroxypropyl guaran and diutan gum, while retarding effect of other admixtures varied only slightly with the amount of biopolymer in the studied range of doses. However the studied admixtures were less effective in the delay of accelerating period, as well as the reduction of total heat generated during the reaction, in comparison with cellulose ethers. Other admixture than hydroxypropyl guar gum or diutan gum should be chosen if the set-retarding ability is not appropriate for the mixture use, otherwise the advantage over cellulose ethers will not be significant.

1. Introduction
Nowadays the use of ready-mix mortars is widely spread due to an easiness of use and reproducibility of the mixture qualities between different mixings. Since the 1960’s the biopolymeric admixtures, namely cellulose ethers, are being used to improve the water retention value, adhesion, and workability of cementitious mixtures [1–5]. The cellulose ethers (CEs) used (most common is hydroxyethylmethyl cellulose (HEMC)) undesirably affect early-age compressive strength [6] and noticeably extend setting time [7].

The process of cellulose refining is also problematic with the current environmentally responsible policies, becomes more and more objectionable. The alternative products based on naturally occurring polysaccharides are being studied for their use as replacement of cellulose ethers in the concrete industry [8]. The biopolymers used come from different environments on Earth. The seaweed biopolymers such as carrageenan (CG) and alginates (salts of alginic acid) are obtained by boiling algae in alkaline solution and are furtherly used without additional chemical improvement. Diutan gum (DG) and xanthan gum (XG) are one of the most used alternatives which improve properties of
self-consolidating concrete (SCC) notably reducing bleeding and segregation [9, 10]. The DG and XG are microbial polysaccharides, meaning, that they are the product of microbes which feed on the nutrient solution in a process called aerobic fermentation. The XG and DG are also used without further chemical improvements. The biopolymers which, similarly to cellulose, are subjected to further chemical modification are chitosan and guar gum. The biopolymers are modified to achieve better solubility in water and alkaline solutions and to improve their behaviour. Guar gum is a galactomannan form the endosperm of beans of Cyamopsis tetragonoloba, a legume widely cultivated in India. Guar gum and its derivatives are widely used mainly in food, textile, and drilling industry [11, 12]. In concrete the addition of guar gum derivatives improves the properties of SCC in similar way to DG and XG [8, 13–15]. Hydroxypropyl guar (HPG) in cementitious mortar increases the water retention value with less efficiency than HPMC [16, 17]. The production of chitosan ethers is the least environmental friendly out of the aforementioned alternatives. Chitosan is mainly obtained from shrimp shells, which are treated with acids to remove mineral constituents (mainly CaCO₃) and with alkalis to remove proteins and to deacetylate the chitin. Lately, more ecological alternatives as enzymatic decomposition of the shells have been studied [18]. The chitosan ethers addition also improves the water retention value of mixture [19, 20]. The hydroxypropyl derivatives of both above-mentioned polysaccharides also showed air-entraining function in the lime-based mortars [21, 22].

Overall the influence of these biopolymers on the properties of building materials is scarcely studied with even less studies in the more specific fields such as affection of hydration reaction. The polysaccharides, in general, have retarding effect on the Portland cement hydration. There are several possible explanations of the phenomenon, the complexing ability of sugars with calcium ions [23, 24] or the chelation, which can be important in the adsorption ability [23, 25]. There is sufficient amount of studies concerning the addition of CEs. The authors agree that the CEs affect the hydration of cement particles, in the calorimetric study, the prolongation of induction period, delay of acceleration period, and reduction of the reaction heat in the acceleration period is observed for different derivatives [26–28]. Similar conclusions were made by A. Peshard et al. [29, 30] concerning the conductometric observations. The conductometry alongside with isothermal calorimetry was also used by T. Poinot et al. [31] to study HPG with different degree of substitution, the HPGs showed higher delay of the beginning of acceleration period than HPMC, but still lower than the one of HEC. The addition of chitosan of different molecular weight led to the delay of portlandite precipitation peak with the delay increasing with growing molecular weight as was conductometrically studied by M. Lasheras-Zubiate et al. [32] Wellan gum, polysaccharide structurally similar to diutan gum, expressed only slight retarding effect in comparison with CEs [33]. Out of other natural polymer-based admixtures studied, the starch ether-based admixture significantly reduced the heat evolution during the acceleration phase with acceptable delay of its beginning [34]. The black gram pulse (one of the India’s widely produced legumes) addition had strongly retarding effect in higher doses, postponing the beginning of acceleration phase by several hours, causing acceptable compressive strength difference for cement mortar after 28 days of curing time [35, 36].

The study aims to compare the influence of the biopolymers mentioned in second paragraph (CG, DG, XG, HPG and hydroxypropyl chitosan (HPCH)) on the kinetics of ordinary Portland cement hydration in normal conditions. The same substituent group for both biopolymer derivatives (HPG and HPCH) was chosen to minimize the influence of different substituent groups observed by O.Z. Hua et al [28] on cellulose.

2. Materials and methods

2.1. Materials

The cement used was CEM I 42.5 R class cement according to EN 196-1 (Carmeuse Czech Republic), the chemical and mineralogical compositions of the cement are presented in table 1. The admixtures of dosage 0.1%, 0.5%, and 1% of cement weight were added to the mixture to study their effect on cement hydration. The admixtures used are summarized in table 2.
Table 1. Chemical and mineralogical composition of cement obtained by XRF analysis and calculated by modified Bogue equation according to ASTM C 150-94 and physical properties of the cement.

| oxide content | oxide | content | property | value | mineral content |
|---------------|-------|---------|----------|-------|----------------|
| CaO 61.48%    | MgO   | 0.86%   | LOI      | 4.17% | C₃S 42.39%     |
| SiO₂ 21.26%   | Na₂O  | 0.12%   | Blaine fineness | 360 m² kg⁻¹ | C₂S 28.97% |
| Al₂O₃ 5.08%   | K₂O   | 0.91%   | specific gravity | 3120 kg m⁻³ | C₃A 7.30% |
| Fe₂O₃ 3.64%   | MnO   | 0.07%   |          |       | C₄AF 11.08%    |
| SO₃ 2.42%     | TiO₂  | 0.29%   |          |       |                |

*a* LOI = Loss on ignition

Table 2. The list of admixtures used in the study.

| admixture used abbreviation | business name (if given) | Supplier / manufacturer |
|-----------------------------|--------------------------|-------------------------|
| sodium salt of alginic acid | ALGNA                    | Sigma-Aldrich, Co.      |
| carrageenan                 | CG                       | Genuvisco CG-131        |
| diutan gum                  | DG                       | Kelco-crete DG-F        |
| hydroxypropyl guar          | HPG                      | BASF Construction Solutions GmbH / CP Kelco |
| hydroxypropyl chitosan      | HPCH                     | Lamberti SpA            |
| xanthan gum                 | XG                       | Kraeber & co, GmbH      |
|                             |                          | Biesterfeld Silcom s.r.o. / CP Kelco |

2.2. Experimental setup, sample preparation

The measurements were executed using TAM Air isothermal calorimeter (TA Instruments). The samples were prepared according to the following procedure: The cement and admixture in specified dose were mixed together and well homogenized. 4 g of dry mixture were precisely measured and put into glass phial. Water to achieve 0.5 water/cement ratio was prepared into specific instrument, which allows mixing and adding water in the closed environment of calorimeter. The ratio of 0.5 was chosen so that even the mixtures with large doses of water-retaining agent can be sufficiently mixed using the implement. The phial with the instrument were put into calorimeter and tempered to 25°C. After the tempering for 24 hours, the water was added to the mixture, it was well mixed and at the same time the measurement was started. The data collection was stopped when the heat flow of all the samples was close to zero.

3. Results and discussion

3.1. Heat flow

The heat flow curves of the cement pastes containing 0.1%, 0.5% and 1% of admixture are presented in figures 1, 2, and 3 respectively. Both peaks, first of initial reaction after introduction of water into cement mixture in the first 30 minutes, and second, the main hydration peak between 2 and 48 hours, are observed in the cut-outs in the figures 1 to 3. The addition of admixture in any dosage with exception of HPG in 0.5% dose decreases the intensity of the heat evolution during this period. Dosage dependency is unclear during this period, only XG with increasing dose decreases the height of the peak. Other admixtures lower the heat evolution the most in certain dose, and in higher or lower dosage the heat evolved is higher. The doses of lowest initial heat evolution are 0.1% for HPG, DG, and CG and 0.5% for HPCH and ALGNA.
Figure 1. The hydration heat evolution of cement pastes with 0.1% of admixture.

Figure 2. The hydration heat evolution of cement pastes with 0.5% of admixture.

Figure 3. The hydration heat evolution of cement pastes with 1% of admixture.
The evolution of main hydration peak, zoomed in the second cut-out, is crucial for the heat evolution during the concrete hardening in the structure, and it also describes the set-retarding function of the admixture. All the admixtures tested showed retarding function expectedly, as they are all of polysaccharidic structure [23–25]. The dosage dependency of the admixtures is more clear in the case of main hydration peak. On the figure 4, the most dosage dependent (HPG), and least dosage dependent (HPCH) admixtures are shown. The dosage dependency of HPG has been observed by T. Poinot et al. [31] as a delay of portlandite precipitation time in conductometric curves, thus prolongation of the period of dissolution of anhydrous phases and precipitation of CSH. The dosage-depency in delay of acceleration phase for HPG and DG is similar to the cellulose ethers [26, 27], but the peak height decrease is lower with the tested admixtures. The HPG and DG are a little bit more efficient than the black gram pulse, causing higher heat flow reduction for the main hydration peak [35, 36]. The retarding effect of ALGNA, HPCH, XG, and CG is comparable to the one of starch ether [32] studied by A. Peshard et al.

![Figure 4](image-url). Heat flow curves illustrating dosage-dependancy of HPG and HPCH addition, numbers representing the dosage in %.

3.2. Total cumulative heat

The cumulative heat evolution for the samples with the highest dose of admixture (1%) is presented in figure 5. The delay of start of acceleration phase of HPG and DG is observed as a delay of onset of the curve. The values at the time-points of 48 hours (the value chosen, because at that time even delayed samples reached similar heat flow, so the main heat-evolution phase is over) and 144 hours are summarized in table 3. The more varying values are seen for the above mentioned biopolymers with retarding function, the other ones like ALGNA or HPCH vary only slightly and the highest difference is observed for the highest dose. If the results are compared with the ones obtained on cellulose ethers, namely HEMC, in the same dosage, the studied biopolymers showed higher heat evolved (not less than 91% of reference value for DG in 0.5% dose in comparison with 84% obtained on HEMC) [26]. The heat evolved in the modified pastes was in average 95% of the heat evolved in the reference paste, the most efficient admixtures HPG and DG did not reach lower than 86.4% and 87.5% respectively for the 48 hours time point. DG is slightly more efficient in comparison with wellan gum (chemically similar polysaccharide with a shorter side-branch), where DG in 0.1% dosage reached 94.9% of heat of reference paste and wellan gum in same dosage and timepoint achieved the value of 97.3% [33].
Table 3. Cumulative heat after 48 and 144 hours of hydration [J g\(^{-1}\)].

| dose/ time | ALGNA | CG | DG | HPG | HPCH | XG |
|------------|-------|----|----|-----|------|----|
| 48h        | 272   | 272| 272| 272 | 272  | 272|
| 144h       | 343   | 343| 343| 343 | 343  | 343|
| 0.1%       | 270   | 263| 258| 266 | 269  | 268|
| 0.5%       | 268   | 260| 250| 250 | 262  | 261|
| 1.0%       | 261   | 257| 238| 235 | 269  | 254|

Figure 5. Total cumulative heat of the samples modified by 1% of biopolymeric admixture.

4. Conclusions
The paper studies the influence of addition of biopolymers on the cement hydration process using isothermal calorimetry. All the biopolymers showed retarding effect as expected due to their polysaccharidic nature. The notable dosage dependency of hydroxypropyl guaran and diutan gum has been observed in the range of doses between 0.1% and 1% of cement weight. Other admixtures studied, as hydroxypropyl chitosan, xanthan gum, carrageenan, sodium alginate showed only little dosage-dependency in comparison with the two above-mentioned admixtures.

While compared to the cellulose ethers, the most used water-retaining admixture to cementitious materials, the retarding effect of the hydroxypropyl guaran and diutan gum is comparable to the one of cellulose ethers. The heat flow reduction of all the biopolymers studied is lower than the cellulose ethers. Sodium salt of alginic acid and hydroxypropyl chitosan were the biopolymers the least affecting the hydration of Portland cement in the studied doses.

Any of the studied admixtures is utilisable to Portland cement-based mixtures as a replacement of cellulose-ether based admixture. Depending on the pertinence of the set-retarding ability the appropriate admixture may be chosen taking into account efficiency in fulfilling the primary goal of the admixture use.

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