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Characterization of aerial lime-based mortars with addition of biopolymers

Characterization of aerial lime-based mortars with addition of biopolymers

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Abstract. The paper studies the influence of addition of viscosity enhancing biopolymers (diutan gum, gellan gum, xanthan gum, carrageenan, and sodium salt of alginic acid) in the doses of 0.1%, 0.5% and 1% on the fresh state, and physical-mechanical properties of hardened mortars. The mortars were prepared with the constant water/binder ratio and the binder/aggregate ratio of 1:3 by weight. The properties have been studied after 7 and 28 days of curing time. All the admixtures, with the exception of gellan gum, improved workability (by lowering the value of spread) in comparison with reference mortar. Most of them also increased the amount of air on the fresh mortar, thus decreasing the density of fresh mortar and also the bulk density of hardened specimens. The addition of biopolymers caused certain decrease of strengths, but there was observable trend of decreasing difference between the reference and tested mortars with the increasing amount of time.

1. Introduction

The viscosity enhancing admixtures (VEA's) are widely used in the building materials especially in concrete and dry mix mortars. Due to a volume of concrete consumption in comparison with lime-based mortars, the most of the studies focus on the influence of wide range of admixtures on the concrete or cement-based pastes and mortars thus the influence of the VEA on the lime mortars is only marginally examined. The most common biopolymer admixtures are cellulose ethers but the use of guar gum, chitosan ethers, diutan gum, and xanthan gum is expanding [1].

The paper studies the influence of, in the building practice, less-known biopolymers on the properties of aerial lime-based mortars. Namely the sodium salt of alginic acid, gellan gum, xanthan gum, diutan gum and carrageenan. The biopolymers used can be diversified in two basic groups: seaweed biopolymers [alginic acid sodium salt (ALGNA), carrageenan (CG)], and microbial (gellan gum (GeG), xanthan gum (XG), and diutan gum (DG)). All of the biopolymers are currently mostly used in the food and drug industry as thickening agents, stabilizers, and gelling agents. [1, 2] The alginates in cementitious material caused notably lower strength decrease in comparison with the commercial super absorbent polymers (SAP) and met the strength demand of cement nominative strength in most cases even though the increased water demand [3]. The alginate added to SCC as a VEA notably reduced bleeding and improved the fresh state properties of mixture [4]. Carrageenan, in building materials, was tested as admixture for fly-ash geopolymer, where its addition considerably increased strengths, mainly by creating more condensed structure [5]. Use of carrageenan in cement-based material is reported only as a foam-stabiliser for preparing extremely porous cementitious foam, where the low strength was mainly caused by porosity and not the biopolymer addition [6]. Gellan gum is used mainly in food and drug industry. In building materials GeG hydrogel slurry was mixed with gypsum or cement slurry to create porous materials. The GeG hydrogel did not affect the reaction of cement nor gypsum in any observable way [7]. On the other hand xanthan gum is used in SCC as VEA, where in certain doses it can eliminate bleeding, reduce segregation, and it does not affect strength of concrete [1, 8]. Diutan gum (DG) is chemically similar to GeG, having same backbone and differing only by substituents on the side chain, thus having different properties. DG is mainly used as VEA in concrete, where it is used for same applications as XG. In comparison with XG the effects of DG addition are independent on temperature or concentration of monovalent and bivalent ions (e.g. Ca^{2+}) in solution thus being more suitable for cement or lime mixtures due to high concentrations of Ca^{2+} cations in the mixtures [4, 8, 9].

The goal of this work is to compare the effects of above-mentioned biopolymers in various doses on the fresh and hardened state properties of aerial lime-based mortar.

2. Materials and methods

2.1. Mixing procedure and materials

The mixture consisted of commercial dry hydrated lime (Carmeuse Czech Republic) of the CL 90 S class according to EN 459-1, the siliceous sand fraction 0-4 mm (Českomoravský štěrk a. s., Hulín, Czech Republic) and the admixture of doses 0.1%, 0.5%, and 1% of binder weight. The admixtures used were: sodium salt of alginic acid (Sigma-Aldrich, co), diutan gum (Kelco-crete DG-F, BASF Construction Solutions GmbH), xanthan gum (Kelzan AP-AS), carrageenan (Genuvisco CG-131), and gellan gum (Kelcogel CG-L-A) three last named supplied by Biesterfeld Silcom s.r.o. but all with exception of alginate being products of CP Kelco. Specimens were prepared by dry mixing of hydrated lime with sand in a 1:1 volumetric ratio, which was converted to 1:3 gravimetric ratio to avoid imperfections, then the admixture was added and all was well-mixed. The dry mixture was added to the specified amount of water (constant water/binder radio of 1.15:1). Prepared mortar was used for test of fresh state properties, and from the rest of the mortar, beams of 40 × 40 × 160 mm were prepared.

2.2. Methods

2.2.1. Fresh state properties. On the fresh mortar, several properties were tested. Flow table test was used to determine workability. Water retention value was stated by weighting water-absorbent material placed under specified amount of mortar for 5 minutes. Density of fresh mortar was recorded by weighting vessel of 1 dm^3 volume filled with mortar. Than content of air in fresh mortar was obtained by using device designed for this type of measurement. All of these tests and instruments were used according to EN 459-2.

2.2.2. Hardened state properties. Bulk density of mortars was stated by measuring and weighting beams before strength test. Flexural strength was determined by three point bending test. Two parts from the test were than tested for compressive strength. These tests were carried out according to EN 1015-11. A piece of sample representing the cross section of the inner part of the beam was milled in mortar mill and used to determine amount of $Ca(OH)_2$ in the samples using differential thermal analysis in combination with thermogravimetric analysis to observe the influence of the admixtures on the carbonation of prepared mortars. The hardened state properties were stated on the specimens 7 and 28 days old stored in laboratory conditions (20±5°C, 50±10% RH) until the day of testing.

3. Results and discussion

3.1. Fresh state properties

Fresh state properties are summarized in Figures 1 and 2. The gellan addition had almost none effect on any of tested properties, this being probably due to its high gel setting point at room temperatures [10]. Other admixtures acted as thickening agents with different dosage-dependant effects. The most effective was DG, which even in small doses dramatically reduced slump. CG had more linear course in slump reduction, both reaching slump of 100 mm in the highest dose, where 100 mm is also inner diameter of the testing cone. Surprisingly low effect of XG addition compared to expectations from concrete usage is most likely caused by its sensitivity to concentration of certain cations in the solution, where lime mortar contains many more Ca^{2+} cations in comparison with cement slurry [8, 9].

The values of air content in the fresh mortar corresponded to the slump reduction with no significant difference, thus we can conclude that the volume of air in the prepared mortars is due to the workability and not the air entraining function of any of the admixtures used as it was in the case of different biopolymers in the literature [11, 12]. The density of fresh mortar is closely-linked with the air content, thus the same conclusion for the mortars behaviour ensues.

Water retention value of lime mortar is generally quite high in comparison with cementitious materials. Decrease of water retention of lime mortar with addition of small dose (0.1%) of some of the admixtures (CG, GeG, and XG) occurred. This phenomenon has been observed on lime mortars also with other admixtures e.g. chitosan ethers or starch [12]. The values reached in the highest dose by the DG and alginate are comparable to the values of chitosan ethers in the same dosage [12]. The highest values obtained with the admixtures are comparable to the values of starch in significantly higher dose on lime mortar or with hydroxypropylmethyl cellulose and hydroxypropyl guar added to cement mortar [11, 13].

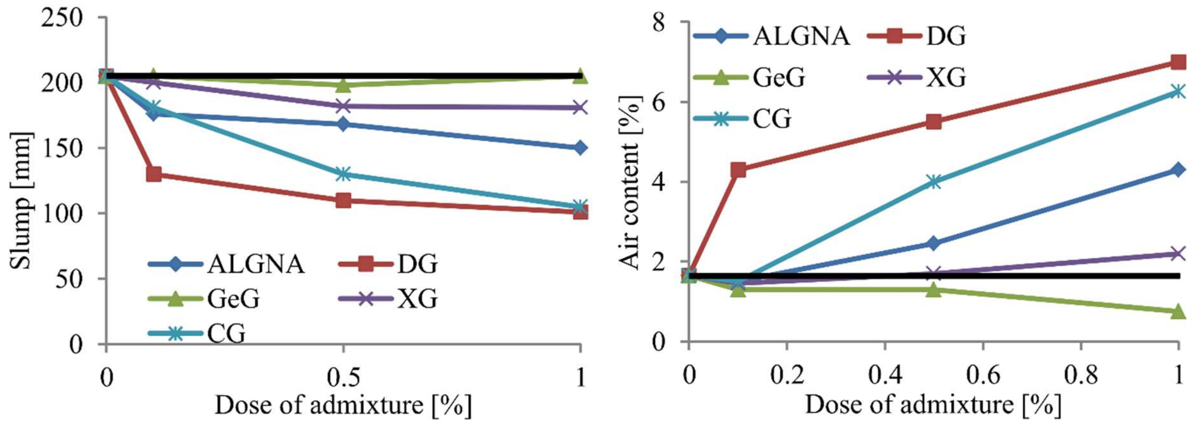

Figure 1. Slump and air content of mortars with biopolymer admixtures.

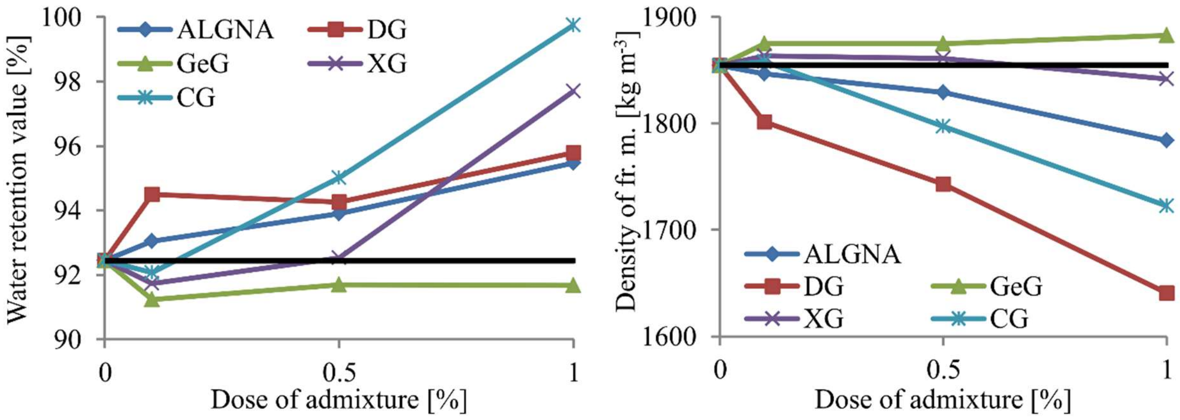

Figure 2. Water retention value and density of fresh mortars with admixtures.

3.2. Hardened properties of lime mortars

3.2.1. Strength properties. Flexural and compressive strength of specimens had been tested after 7 (Figure 3) and 28 (Figure 4) days of curing time. As seen in Figure 3, the addition of admixture caused notable decrease of early age strength, which is in accordance with results with different admixtures in the literature [11, 14]. The significant improvement, especially in the flexural strength results, is typical for lime mortar [11] and probably caused by different humidity characteristics of the specimens with different admixtures and doses. The dosage dependence in the case of XG and GeG is not as obvious as in the case of other biopolymers.

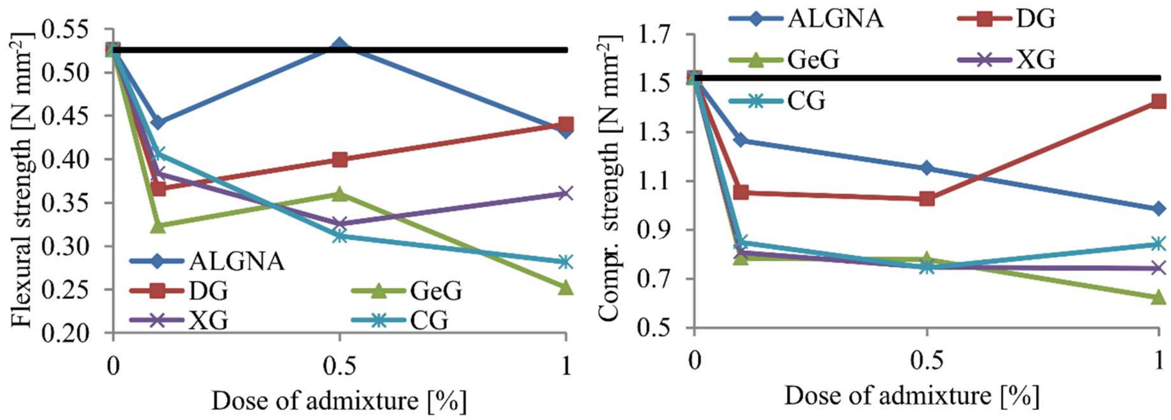

Figure 3. Flexural and compressive strength of 7 days old specimens.

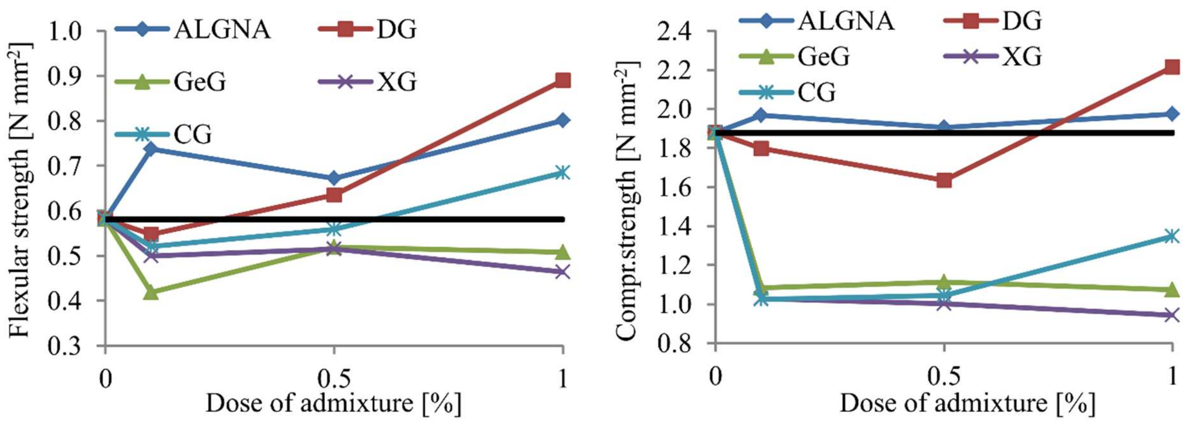

Figure 4. Flexural and compressive strength of 28 days old specimens.

Alginates and diutan gum were the best performing admixtures, both showing distinctly lower decrease of strength in the first 7 days, and after 28 days of curing time, the mortars with these admixtures reached similar or even higher values of strength than the refference mortar. The development of strength of mortars with CG is remarkable, at 7 days the strength values were ones of the lowest, but after 28 days CG in highest dose in case of flexural strength surpassed the refference mortar and even for the compressive strength there was perceptible growth of difference with other badly performing admixtures. XG and GeG confirmed their insuitability when used in lime mortar as it was seen even from the fresh mortar properties. Both of them significantly decreased strenghts of mortars with no hint of improvement in later ages.

3.2.2. Carbonation rate. The amount of free water, $Ca(OH)_2$, and $CaCO_3$ were studied using diferential thermal analysis in combination with thermogravimetry. Table 1 states the amount of free water in the mortar specimens. As we can see, the humidity of 7 days old mortars vary depending on the type of admixture and its dose. With increasing dose of admixture the humidity of specimen also increased. The samples with alginate were the most humid and XG samples showed the lowest humidity. Humidity of 28 days old samples was varying around similar values in the case of all admixtures. The amount of water retained in the mortar by the admixtures can decrease the short term strength as observed in Figure 3 (lime mortar obtains initial strengths mostly by drying) but also the increase of the strength in 28 days for the carbonation reaction is in solution [15].

Table 1. Amount of free water contained in mortar samples after 7 and 28 days of curing time.

	REF	ALGNA 1	ALGNA 5	ALGNA 10	DG 1	DG 5	DG 10	GeG 1	GeG 5	GeG 10	XG 1	XG 5	XG 10	CG 1	CG 5	CG 10
free H_2O [%] 7d	0.48	1.45	3.33	7.54	0.42	0.69	2.28	0.45	0.57	1.35	0.40	0.63	0.53	0.29	0.80	3.01
free H_2O [%] 28d	0.45	0.35	0.28	0.26	0.30	0.39	0.35	0.38	0.39	0.41	0.43	0.45	0.39	0.27	0.31	0.27

The difference in percentage representation of $Ca(OH)_2$ and $CaCO_3$ is shown in Figure 5. The decrase of amount of $Ca(OH)_2$ as well as increase of $CaCO_3$ are proofs of the ongoing carbonation reaction. From the Figure 5 we can see that only ALGNA in two lower doses slightly slowed carbonation reaction between 7 and 28 days. This can be caused by aprreciable amount of humidity in 7 days old samples because the humidity also partially influences the difussion of CO_2 into the mass of specimen. If the strength results shown in Figures 3 and 4 were also taken into account it can be assumed, that the strength of ALGNA specimens is not much affected by the slowed carbonation.

The masive increase of $CaCO_3$ content in the samples with the highest dose of carageenan can also explain the notable difference between 7 and 28 days strength of this mortar. From the results obtained we can assume that the bipolymer addition to the lime mortar did not slow carbonation reaction, and it appeared to be beneficial for it.

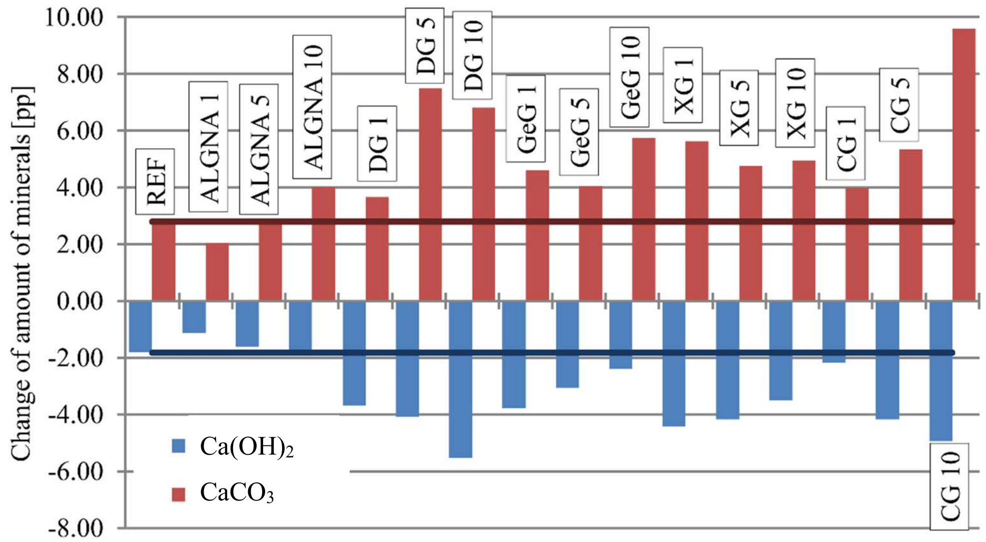

Figure 5. Change of amount of $Ca(OH)_2$ and $CaCO_3$ in samples between 7 and 28 days.

4. Conclusions

The paper studied the influence of several different biopolymers on the properties of aerial lime-based mortar. The mortars were prepared with constant water/binder and binder/aggregate ratios. The properties of mortars varied with the type and dosage of the admixture.

In the fresh state most of the admixtures acted as thickening agents with different effectiveness. The only exception was gellan gum, for it had no significant impact on the properties of the mortar. The results of air content in the fresh mortar as well as density of fresh mortar were corresponding with the results of the flow table test, thus none of the admixtures showed air-entraining function while used in the aerial lime-based mortar. The water retention value was slightly decreased by the CG and XG in the lowest dose, but with the increasing dosage the values had increased significantly, especially for carrageenan, which performed best in the highest dosage.

All of the admixtures lowered strengths after 7 days; this may be caused by the water-retaining function of the admixtures. After 28 days of curing time the ALGNA, DG, and CG showed results comparable with reference mortar for flexural strength, but the carrageenan mortar still presented significant decrease of compressive strength. Decrease of amount of $Ca(OH)_2$ and increase of amount of $CaCO_3$ in the specimens was higher than in the reference mortar for all specimens with exception of ALGNA in any dosage. This indicates slightly beneficial effect of biopolymer addition on the carbonation reaction.

ALGNA, DG and CG showed interesting results and are to be studied in the future. The effect of addition of XG is discussable and its future research is to be well considered. Gellan gum had no impact on the fresh state properties of lime mortar and significantly decreased strengths of the mortar, thus it is not suitable for the use in the lime mortars in the way presented in this paper.

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References

[1] Plank J 2004 *Appl. Microbiol. Biotechnol.* **66** pp 1–9
Singh NK, Mishra PC, Singh VK and Narang KK 2003 *Cem. Concr. Res.* **33** pp 1319–29
[2] Rinaudo M 2008 *Polym. Int.* **57** pp 397–430
[3] Mignon A, Snoeck D, D'Halluin K, Balcaen L, Vanhaecke F, Dubruel P, Van Vlierberghe S and De Belie N 2016 *Costr. Build. Mater* **110** pp 69–74
[4] Bezerra U T 2016 *Biopolymers and Biotech Admixtures for Eco-Efficient Construction Materials* (Duxford: Woodhead Publishing)
[5] Li Z and Zhang L 2016 *Biopolymers and Biotech Admixtures for Eco-Efficient Construction Materials* (Duxford: Woodhead Publishing)
[6] Akthar F K and Evans J R G 2010 *Cem. Concr. Res.* **40** pp 352–8
[7] Rutkevičius M, Munusami S K, Watson Z, Field A D, Salt M, Stoyanov S D, Petkov J, Mehl G H and Paunov V N 2012 *Mater. Res. Bull.* **47** pp 980–6
[8] Isik I E and Ozkul M H 2014 *Constr. Build. Mater.* **72** pp 239–47
Vazquez A and Pique T M 2016 *Biopolymers and Biotech Admixtures for Eco-Efficient Construction Materials* (Duxford: Woodhead Publishing)
[9] Van Der Vurst F, Grünewald S, Feys D, Lesage K, Vandewalle L, Vantomme J and De Schutter G 2017 *Cem. Concr. Compos.* **82** pp 190–201
Xu L, Gong H, Dong M and Li Y 2015 *Carbohydr. Polym.* **132** pp 620–9
Roca C, Alves V D, Freitas F and Reis M A M 2015 *Front. Microbiol.* **6** 288
[10] Kang K S, Veeder G T, Mirrasoul P J, Kaneko T and Cottrell I W 1982 *Appl. Environ. Microbiol.* **43** pp 1086–91
[11] Izaguirre A, Lanas J and Álvarez J I 2011 *Cem. Concr. Compos.* **33** pp 309–18
Žižlavský T, Vyšvařil M, Bayer P and Rovnaníková P 2018 *Key Eng. Mater.* **760** pp 22–9
Vyšvařil M, Hegrová M and Žižlavský T 2018 *Key Eng. Mater.* **760** pp 257–65
[12] Vyšvařil M and Žižlavský T 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **251** 012039
[13] Izaguire A, Lanas J and Álvarez J I 2010 *Carbohydr. Polym.* **80** pp 222–8
Lasheras-Zubiate M, Navarro-Blasco I, Fernández J M and Álvarez J I 2012 *Cem. Concr. Compos.* **34** pp 964–73
[14] Izaguirre A, Lanas J and Álvarez J I 2010 *Cem. Concr. Res.* **40** pp 1081–95
[15] Shoh S-M, Ho C-S, Song Y-S and Lin J-P 1999 *Ind. Eng. Chem. Res.* **38** pp 1316–22
Van Balen K and Van Gemert D 1994 *Mater. Struct.* **27** pp 393–8