INVESTIGATION OF GEOPOLYMER BINDERS WITH RESPECT TO THEIR APPLICATION FOR BUILDING MATERIALS

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Geopolymer binders based on a commercial metakaoline, water glass and sodium hydroxide have been investigated with respect to their application for building materials. Mixture compositions with favourable properties could be identified. For the production of building materials, a process technology at ambient temperature may be less feasible due to delayed setting and strength evolution. Therefore curing at elevated temperatures was tested. A heat treatment at 75°C for 4 hours yields satisfactory results. With this production technology geopolymer binders seem to be suitable for selected building materials like reinforced particle boards. This is on the one hand due to a long processing time together with a rapid strength development during temperature treatment. On the other hand they develop desirable properties like water resistivity, limited shrinkage and sufficient strength values.

INTRODUCTION

Geopolymer binders from various raw materials are well known since decades and investigated by several authors [1-12]. A survey of the knowledge in this field can e.g. be found in [2, 3, 12.]. The investigations documented here had the goal to test their suitability for several shaped building materials like e.g. wood fibre reinforced particle boards. For this application a water resistant binder with sufficient strength is desirable. Moreover the production technology necessitates an adequate processing time. Nevertheless after the shaping procedure the materials should be demoulded immediately to enable a feasible production. Therefore the binder should show a rather late beginning of setting, but it should be possible to accelerate strength evolution when the material is shaped.

EXPERIMENTAL

Geopolymer binders were prepared from commercial metakaoline (product name "AGS" from company AGS BMP., Clérac, France), containing 54.5 wt.% SiO_2 and 39.5 wt.% Al_2O_3, with a bulk density of 559 kg/m^3, a d_{50}-value of 18.6 µm (50 wt.% <18.6 µm) and a specific surface area of 16 m^2/g according to the BET method. Alkali-activation was performed with NaOH (50 wt.%) and water glass solutions having a silica modulus (mass ratio SiO_2/Na_2O) of 3.38 and containing 8 wt.% Na_2O. A variety of geopolymer compositions with different oxide ratios were tested. Table 1 presents a selection of mixtures with their chemical compositions represented by the molar oxide ratios SiO_2/Al_2O_3 (S/A), Na_2O/Al_2O_3 (N/A), Na_2O/SiO_2 (N/S) and H_2O/Na_2O (H/N). For mixtures with N/S >0.296 solid water glass was added, too.

At first the influence of the mixing procedure and the temperature during setting on the properties of the resulting geopolymers were investigated. Two methods for preparation have been chosen:

- Method A: The sodium hydroxide and water glass solutions were mixed, and within 30 seconds metakaoline was added, succeeded by a thoroughly mixing of the paste. Then the paste was formed into specimens of 40×40×160 mm in size and cured in moulds during 24 hours at ambient conditions (20 ± 2°C, 65 ± 5% r.h.). After this time a curing of the demoulded specimens at ambient conditions and under water (20 ± 2°C), respectively, until testing followed.
- Method B: In a first step the sodium hydroxide and water glass solutions were mixed and cooled down to 20 ± 2°C after their exothermic reaction. Then metakaoline was added and the paste was mixed thoroughly. Again specimens of 40×40×160 mm in size were formed. The curing procedure used was heating up to 60, 75, and 90°C, respectively, for a duration of 2 and 4 hours, followed by a storage at ambient conditions (20 ± 2°C, 65 ± 5 % r.h.) in moulds for 24 hours. The specimens were demoulded and stored at 20 ± 2°C alternatively at 65 ± 5 % r.h. and under water until the testing age of up to 28 days.

The geopolymers were characterized by testing the strengths, e.g., compressive strengths, according to [13] after storage for a period of 28 days. Also the changes in weight and length [14] of the specimens in dependence on the storage conditions were determined as well as the Young's modulus. For measurement of Young's modulus a resonant frequency technique was applied. The setting times of the pastes were determined according to [15].

RESULTS AND DISCUSSION

The setting times for pastes of compositions 1-10 (table 1) prepared via method A and the compressive strengths of the geopolymer specimens in dependence on the curing conditions after a period of 7 days are summarized in table 2.

The composition 10 has the highest molar oxide ratio of N/S and H/N. Due to the limited solubility additional solid water glass had to be added. Also enough water was added for preparing a paste with acceptable workability. Both led to a lower heat evolution and in consequence to a delay of setting. Setting started after more than 10 hours. It seems that the ratio of H/N effects the setting of the geopolymer binders. Its influence on the setting can be seen by comparison of compositions 4 and 5. The composition 4 has a H/N-ratio twice of composition 5 and shows delayed setting which starts after more than 10 hours. On the other hand the compositions 1, 5 and 8 have the lowest values for H/N and also show the lowest values for the setting times, for the begin as well as for the end (table 2). The begin of setting and the end of setting show a coefficient of correlation *r* with the ratio of H/N of 0.86 and 0.91, respectively.

Table 1. Molar oxide ratios of primary mixtures forming geopolymer binders.

composition	S/A	N/A	N/S	H/N
1	4.49	1.29	0.287	10.1
2	4.01	1.16	0.290	13.1
3	3.63	1.04	0.286	12.0
4	3.55	1.04	0.295	20.0
5	3.55	1.04	0.295	10.5
6	3.69	1.16	0.314	13.0
7	3.64	1.02	0.281	13.7
8	3.34	0.84	0.251	9.93
9	3.33	0.83	0.248	13.3
10	4.50	1.57	0.349	10.3
range	3.33-4.50	0.83-1.57	0.248-0.349	9.92-20.0

Table 2. Setting times (t_b begin of setting, t_e end of setting) and compressive strengths σ_c tested 7 days after storage at ambient conditions (a) and under water (w)

composition	t_b (min)	t_e (min)	$\sigma_{c,7,a}$ (MPa)	$\sigma_{c,7,w}$ (MPa)
1	30	45	50.8	45.9
2	70	126	27.4	19.6
3	50	115	40.3	30.0
4	> 600	-	2.4	1.6
5	40	52	48.5	38.8
6	140	230	53.3	42.8
7	140	195	63.0	40.5
8	30	50	62.7	52.3
9	155	200	68.2	52.9
10	>600	-	0.1	0

A delayed setting is accompanied by low strength values as can be seen e.g. for compositions 4 and 10 (table 2). The results for the compressive strengths of the geopolymer binders after curing at ambient conditions for a period of 7 days range from 0.1-69 MPa (table 2). Again an influence of the molar oxide ratios of the compositions (table 1) is evident. The compressive strength tends to rise with decreasing molar oxide ratio N/S. The coefficient of correlation *r* for the compressive strength with the ratio N/S is -0.71 after storage at ambient conditions and -0.70 after storage under water. Compared with ambient conditions storage under water results in lower strengths values. The specimens stored at ambient conditions showed cracks which were caused by the shrinkage during curing.

It was observed that the heat evolution was more intense for rather low H/N-ratios. This was believed to have a negative impact on the formation of cracks and the strength. Also the setting times of some compositions were very low with respect to an application as a building material. To grant even conditions for the preparation of geopolymer binders the method B quoted above was developed. The aim of this procedure was to obtain controlled setting and strength development at constant temperature, thus also preventing the formation of cracks. Hereby the pastes were mixed without showing significant heat evolution.

In a first step mixtures 7 and 9 which showed the highest compressive strengths if prepared according to method A were processed as quoted above for method B, but without any heat treatment. Instead of this they were cured in moulds at 20 ± 2°C and 65 ± 5% r.h. Under these conditions the mixtures set relatively slow. After 24 hours composition 7 was still deformable. For composition 9 setting started after 10 hours and was finished after 1.5 more hours. So the setting began four times later than for pastes prepared via method A. In comparison to the strengths of geopolymers from composition 7 and 9 prepared via method A the compressive strengths tested after a period of 7 days were markedly decreased. The compressive strength of specimens from mixture 7 was 22.2 MPa after storage at ambient conditions and 24.4 MPa after storage under water. Composition 9 showed compressive strength values of 41.3 MPa (cured at ambient conditions) and 41.6 MPa (cured under water), respectively. All samples stored at ambient conditions showed large cracks, but none were observed for samples stored under water. The crack formation seems to be a consequence of desiccation prior to the formation of the geopolymer structure.

To avoid this a curing procedure including a thermal treatment was developed and carried out as described above for method B. A thermal treatment was also applied for other investigations [5-7]. Hence, no cracking of the specimens was observed. The results for the compressive strengths after 7 and 28 days of specimens of composition 9 (table 1) in dependence on the thermal treatment and storage conditions are given in table 3. The compressive strengths range from 18.4 - 39.8 MPa.

For a heat treatment at 75°C further investigations have been performed. The changes in weight, in length and the Young's modulus have been measured in dependence of time and the duration of the heat treatment. The results can be seen from tables 4, 5, and 6, respectively. From these investigations the following can be concluded: As can be seen from table 3, for 75°C a duration of 4 hours of the heat treatment results in higher strength values than 2 hours under all conditions. This may be attributed to a higher degree of the binder reaction. Together with table 5 it may be followed that this reaction is accompanied by a volume expansion. For curing under water, the specimens with 2 hours heat treatment show a higher expansion than those with 4 hours heat treatment. Under ambient conditions the expansion due to the residual binder reaction becomes superimposed by a shrinkage due to desiccation, which results in a final shrinkage after 28 days. In the case of the shorter heat treatment the expansion period lasts longer due to the lower degree of reaction achieved by

Table 3. Compressive strengths σ_c for composition 9 after thermal treatment at 60°C, 75°C and 90°C for 2 and 4 hours, respectively, and storage at ambient conditions and under water, respectively, until testing after 7 and 28 days.

	$\sigma_{c,7}$ (MPa)						$\sigma_{c,28}$ (MPa)					
	ambient conditions			under water			ambient conditions			under water		
t (h)/*T* (°C)	60	75	90	60	75	90	60	75	90	60	75	90
2	31.3	28.9	30.3	31.1	22.3	31.4	37.8	29.4	36.9	34.4	18.4	25.1
4	30.6	34.0	32.1	25.0	28.8	19.9	34.3	39.8	32.8	28.7	28.4	26.7

Table 4. Change in weight $\Delta m/m_0$ of specimens of composition 9, thermally treated at 75°C for 2 and 4 hours, respectively, and stored over a period of 28 days at ambient conditions and under water, respectively.

	$\Delta m/m_0$ (wt.%) after *x* days									
	ambient conditions					under water				
t (h)/*x* (days)	1	3	7	14	28	1	3	7	14	28
2	0	-	-	-	-20.1	0	-1.00	-1.20	-1.50	-1.73
4	0	-9.83	-17.2	-20.4	-20.8	0	0.95	1.07	1.05	1.11

Table 5. Change in length $\Delta l/l_0$ of specimens of composition 9, thermally treated at 75°C for 2 and 4 hours, respectively, and stored over a period of 28 days at ambient conditions and under water, respectively.

	$\Delta l/l_0$ (mm/m) after *x* days									
	ambient conditions					under water				
t (h)/*x* (days)	1	3	7	14	28	1	3	7	14	28
2	0	-	-	-	-20.1	0	-1.00	-1.20	-1.50	-1.73
4	0	-9.83	-17.2	-20.4	-20.8	0	0.95	1.07	1.05	1.11

Table 6. Young's modulus *E* of specimens of composition 9, thermally treated at 75°C for 2 and 4 hours, respectively, and stored over a period of 28 days at ambient conditions and under water, respectively.

	E (GPa) after *x* days									
	ambient conditions					under water				
t (h)/*x* (days)	1	3	7	14	28	1	3	7	14	28
2	4.82	4.65	4.57	4.94	7.19	4.82	4.88	4.95	5.02	5.15
4	9.20	8.45	7.12	7.21	7.62	9.22	9.08	9.06	9.01	9.07

the heat treatment. This lower degree of the reaction may also be seen from table 4. In the case of water storage for a curing time of 2 hours at 75°C specimens show a negative mass change which may be explained by the solution of still non-reacted alkalies and other components of the water glass. Contrary to this, for 4 hours curing time the mass of the specimens is in-creased by absorption of water. The Young's modulus of specimens kept under water is higher for 4 hours curing time and remains nearly constant. For 2 hours curing time there is a slight increase due to the residual reaction. Specimens kept at ambient conditions may be subjected to desiccation and to residual geopolymerisation. For 2 hours curing time, the latter is expected to dominate the effect on Young's modulus, resulting in an increase after 28 days. Contrary to this, for 4 hours curing time the chemical reaction is nearly completed and the desiccation results in a decrease of Young's modulus after 28 days.

CONCLUSIONS

The investigations documented here showed both favourable compositions of geopolymeric binders based on metakaoline and conditions for the preparation of specimens. Processing at ambient temperature may be unfeasible due to a delayed beginning of setting. A thermal treatment can avoid this disadvantage. Curing at 75°C for 4 hours resulted in satisfactory properties. Under these conditions, the major part of the geopolymerisation is finished and the material does not need any special secondary treatment. Together with a process technology using elevated temperatures geopolymer binders seem to be favourable for selected building materials. At ambient temperatures they enable a long processing time due to the delayed begin of setting. A thermal treatment yields a rapid strength development necessary for a feasible manufacturing process. The properties investigated here may be suitable for various applications.

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VÝZKUM GEOPOLYMERNÍCH POJIV PRO POUŽITÍ VE STAVEBNÍCH MATERIÁLECH

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Geopolymerní pojiva na bázi komerčního metakaolinitu, vodního skla a hydroxidu sodného se zkoumaly pro jejich možné použití ve stavebních materiálech. Vybraly se směsi složek s výhodnými vlastnostmi. Pro výrobu stavebních materiálů se zdá zpracování při obvyklé teplotě těžko proveditelné díky pomalému tuhnutí. Testovalo se proto zrání při zvýšené teplotě. Uspokojivé výsledky dalo zpracování při 75°C po dobu 4 hodin. Na jedné straně je tedy třeba delšího času zpracování a zahřívání k rychlejšímu vzniku pevnosti. Na druhé straně takto zpracované hmoty mají lepší odolnost proti vodě, menší smrštění a dostatečnou pevnost.