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FROST RESISTANCE OF ALKALI-ACTIVATED CONCRETE WITH DIFFERENT COMPOSITIONS – PARAMETRIC STUDY

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Abstract

Alkali-Activated Materials (AAM) are often considered to be very durable and also frost-resistant. However, there are also contrary experiences. This paper focuses on the frost resistance of AAMs of different compositions – different amounts of activator and different ratios between alkali (R_2O) and silicon oxide content. Sodium water glass was used as the activator and its silicate modulus was modified by the addition of KOH. The R_2O content was 4 -10 % and the R_2O/SiO_2 weight ratio was 33/67 (water glass only) up to 100/0 (KOH only). The frost resistance index was tested at the ages of 28, 91 and 365 days. Specimens were cured in foil or water and comparative specimens were also stored in foil or water.

The results obtained are inconclusive. Firstly, when the reference specimens are stored in water, their bending strength decreases. This means that the frost resistance index is dependent on the use of the reference specimens – better results of frost resistance index are obtained for water-cured beams as reference specimens as they show lower strengths. The composition has a marginal effect on the frost resistance. Longer curing times also do not increase frost resistance.

Keywords:

Alkali-Activated Materials;
Frost resistance;
Strength.

1 Introduction

Current social development and requirements for the sustainability of construction bring new requirements on building materials New types of concrete are among the most important building materials. Concrete has become a popular material, where the benefits include a good combination of affordability and useful properties. When designing structures and structural elements, variants of reinforced concrete [1] and prestressed concrete [2], or concrete elements reinforced with fibres [3,4] are often used. Among the critical aspects of the design of building structures are not only the consideration of basic design criteria, but also the requirements for durability [5] and lifetime period. Extensive concrete research includes mainly materials engineering, which focuses on composition design and optimization. This is mainly the area of HPC (High Performance Concrete) [6] and UHPC (Ultra High Performance Concrete) [7], fibre reinforced concrete, special concretes, concretes for additive technologies, concretes with recycled materials [8] and many other variants. A comprehensive description of properties is essential for the design of building structures.

These are, for example, compressive strength, modulus of elasticity, splitting tensile strength, bending tensile strength. Properties with regard to durability are also important, including scaling resistance, frost resistance etc. A comprehensive description of properties is especially important in cases where advanced numerical modelling is applied in design based on nonlinear analysis. Important areas of research also include load tests of structural elements, which verify in particular the mechanism of failure and the actual collapse of the structure. Key aspects that require attention in the field of concrete include finding alternatives to cement. This is because the production of cement is highly energy-intensive and the total share of CO_2 emissions is order of several percent. Attention is often directed to alkaline-activated materials – AAM [9-12]. The presented paper is also focused on the mentioned area.

Frost resistance is one of the most important aspects of the durability of concrete. It can be divided into two basic processes: 1) internal cracking, which affects concrete strengths and other mechanical properties and 2) surface scaling, which deteriorates the surface of concrete. Both of these mechanisms are affected by the formation of ice in the pores of the concrete. It is well known that the volume of water increases during freezing [13, 14]. This means that if the pores in the concrete are filled with water and the water freezes, the hardened concrete is exposed to internal stress. This stress generally causes deterioration of concrete if the degree of pore saturation is higher than 85 % [15, 16]. The water-to-cement (binder) ratio plays a major role in the porosity and strength of OPS-based concrete. The situation is more complex for alkali-activated concretes (AAC). In addition to the water/binder ratio, the type and dosage of the activator are also essential. This is also the reason for different opinions on the frost resistance of AAC. Cyr and Pouhet [17], regarding sources, show that the frost resistance of AAC is usually considered excellent and that in the case of water glass and especially hydroxide activators, the solution/slag ratio has a significant effect. On the other hand, Bilek et al [18, 19] or Tekle et al [20] have pointed out some issues with the frost resistance of AAC. These papers indicate the positive effect of alkali content up to a specific limit on the frost resistance of AAC as well as the positive effect of air-entraining. This research and article are focused on the effect of different compositions of fine-grained AAC on frost resistance. Since different compositions and dosages of AAC activators provide different mechanical properties, they are likely to affect frost resistance as well, when the was also presented at the conference [21].

2 Experimental setup

Alkali-activated mortars (fine-grained concrete) were prepared from ground-granulated blast furnace slag produced in the Czech Republic, common sand 0/4 mm for concrete production and drinkable water [22]. The mass of slag was kept at 450 g/l of concrete. Sodium water glass with silicate modulus $M_s \approx 2$ (mass percentage 16.5 % Na_2O, 32 % SiO_2, 51.5 % water) was used as an activator in combination with a 50 % solution of KOH. The reason for using KOH in the activator modification instead of NaOH is that the presence of potassium ions enhances the workability of AAM. Mortars with different R_2O contents (% from the mass of slag) and different R_2O/SiO_2 mass ratios were prepared according to the design of the experiment, see Table 1. The water-to-slag ratio was kept constant – w/s = 0.55.

Table 1: Design of Experiment ($R_2O = Na_2O + K_2O$) [22]

		R_2O/SiO_2				
		34/66	**50/50**	**60/40**	**70/30**	**100/0**
R_2O	4 %	X		X		X
	6 %	X	X	X	X	X
	8 %	X		X		X
	10 %			X		X

Fine-grained concretes were mixed in a laboratory mixer with a volume of 10 litres. Firstly, liquid compounds and slag were put into the mixer. After 30 seconds, sand was added continuously for an additional 30 seconds. The mixture was mixed for another 3 minutes. The mini cone flow was measured immediately after mixing. The mixture was then poured into moulds. Prisms 160x40x40 mm were made. The moulds with concrete were covered with foil to prevent water evaporation. The prisms were unmoulded at the age of 1 day (or 2 days in case of R_2O/SiO_2 =100/0). All prisms were wrapped in PE-foil to avoid water exchange with the environment.

The prisms were later used to test the three-point bending strength f_b and compressive strength on fragments of the prisms f_c. The testing of the prisms was performed according to the scheme in Figure 1. Three specimens were tested at the age of 28 days. At the same time, three more specimens were placed in an automatic freezer for 125 freezing and thawing (F&T) cycles. One F&T-cycle represents 4 hours at air -20°C and 2 hours in water at +20°C (according to the Czech norm CSN 73 1322 Determination of Frost Resistance of Concrete). This means that the specimens were exposed to water. This is why 3 more specimens were exposed to +20°C water. These last specimens were tested at the end of the cycles and they can serve as reference specimens for the cycled specimens. However, during cycling, which takes 30 days, even the foil-wrapped specimens may show some strength development. This means that the three other foil-wrapped specimens were tested after the cycles and can also be used as reference specimens. Frost resistance is assessed by the frost resistance index, which is the ratio of the properties of the cycled specimens to those of reference specimens. In this paper, three groups of reference specimens can be used: 1) those tested at 28 days of age in foil, 2) those stored for an additional 30 days in water, and 3) those stored for an additional 30 days in foil.

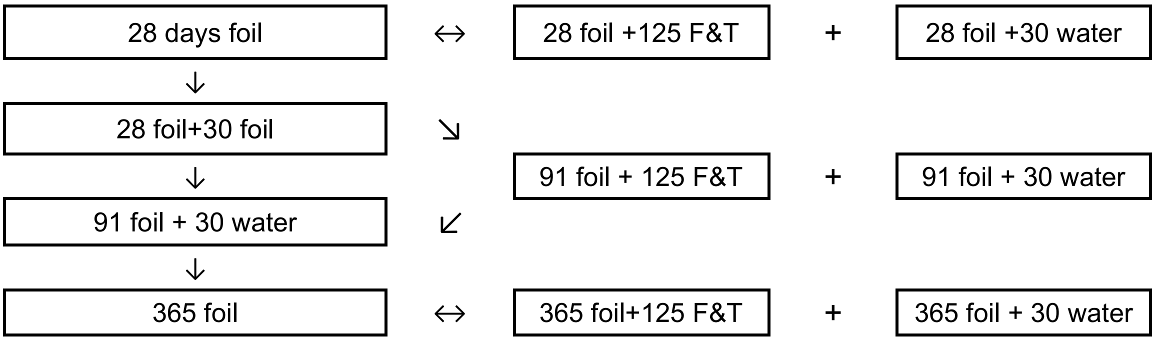

Fig. 1: Schedule of testing. [21]

2 Results and Discussion

2.1 Strength development - example

As an example, Figure 2 shows the compressive strength development for concrete with 6 % of R_2O and R_2O/SiO_2 = 60/40 and Figure 3 the bending strength development.

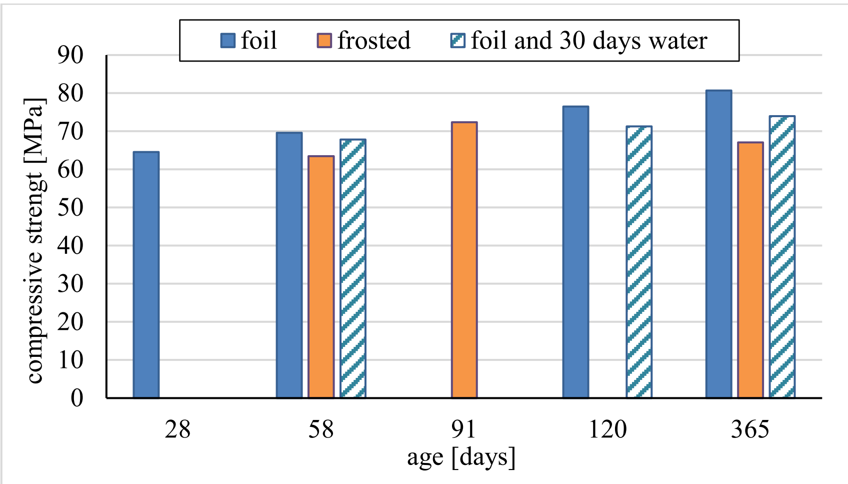

Fig. 2: Compressive strength development; R_2O = 6 % and R_2O / SiO_2 = 60/40. [22]

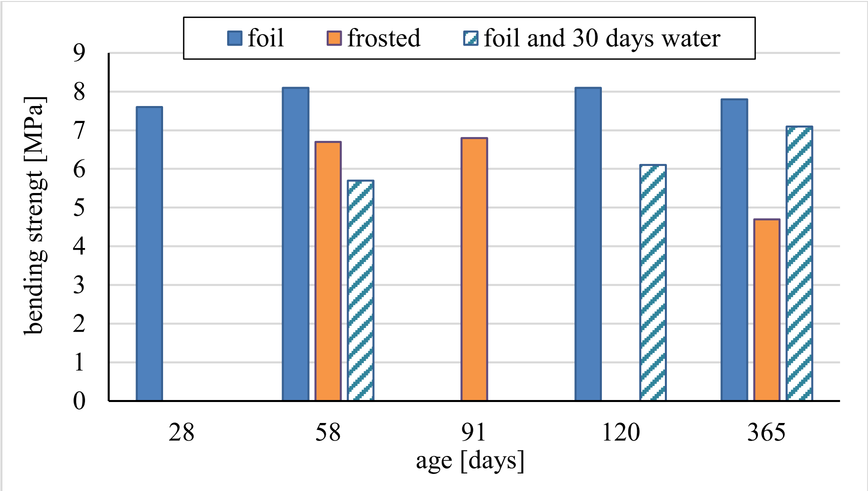

Fig. 3: Bending strength development; R_2O = 6 % and R_2O / SiO_2 = 60/40. [22]

There is a continuous increase in compressive strength in foil-wrapped concretes. Probably there is enough water inside the concrete (*w*/*s*=0.55) to provide the hardening of the concrete. The compressive strength of the frosted beams is similar to that of the foil-wrapped ones at the age of 28 and 91 days. The compressive strength of the additionally water-cured specimens is also similar, but always slightly lower than that of the foil-wrapped specimens. At 365 days of age, the compressive strength of the frosted beams is significantly lower than that of the foil-wrapped beams.

The situation is different in the case of bending strength- see Figure 3. The strength of the foil-wrapped beams increases during the first 60 days and is almost constant thereafter. The bending strength of the frosted beams is always lower than that of the foil-wrapped beams. Also, additionally water-cured beams show significantly lower strength than foil-wrapped beams. This means that it is very important which strength is taken as the reference strength in frost resistance index computing.

2.2. Strengths of AAC with different composition

Similar results to those presented in the previous section were obtained for all the prepared concretes. A general overview up to 91 days can be seen in the following figures. Figure 4 shows the compressive strength of the foil-wrapped specimens (designation 28) with different compositions. It is evident that the concretes with R_2O/SiO_2 = 60/40 and R_2O content higher than 4 % show the highest strengths at 28 days. This agrees with previous results [23].

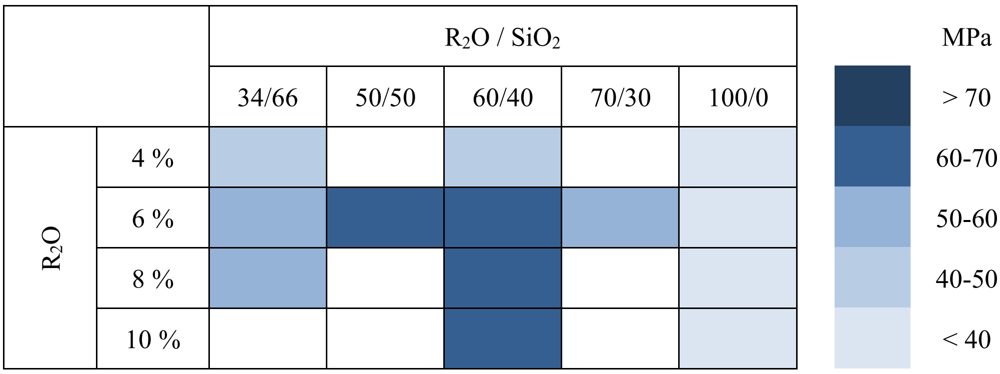

Fig. 4: Compressive strength of concretes – specimens wrapped in foil (designation 28). [22]

A further increase in strength over the next 30 days is shown in Figure 5. There is a clear increase in compressive strength for all mixtures with R_2O higher than 4 except the one with R_2O/SiO_2 = 100/0. Concretes activated with KOH alone exhibit very low strengths

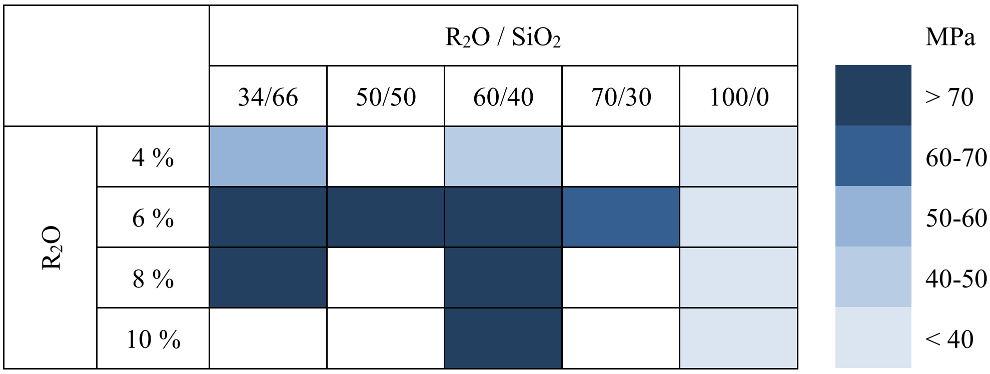

Fig. 5: Compressive strengths – specimens wrapped in foil for 28 days and also in foil during F&T cycles (designation 28+). [22]

Figure 5 can be compared with Figure 6, which shows the compressive strengths of specimens cured in foil for 28 days and then for a further 30 days - during F&T cycles - in +20°C water. Concretes with R_2O = 6% show lower strengths than those cured only in foil. This is quite interesting. One cause may be the inner pressure of the pores filled with water during loading, another may be some leaching of the alkali activator. The gradual degradation of strength may be due to the low stability of sodium aluminosilicate gel in water, as reported for example by Yao et al. [24] Also Chi [25] does not consider water curing to be the most suitable, preferring curing at 80 % humidity. In every case, additional water curing has no positive effect on the compressive strength.

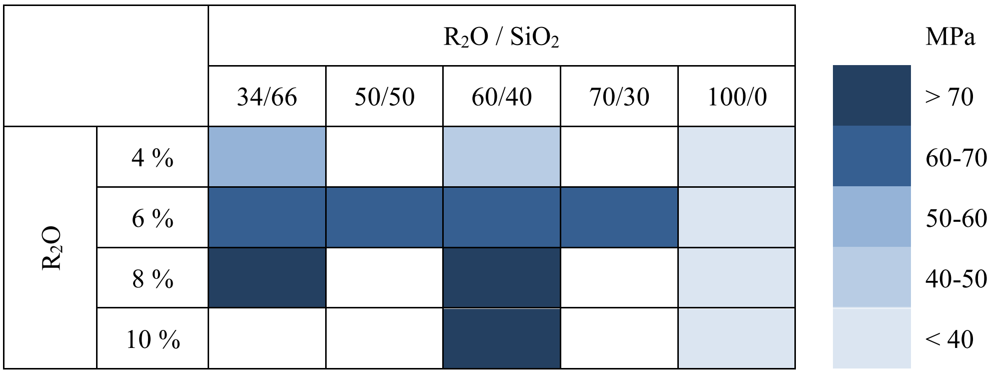

Fig. 6: Compressive strengths –specimens wrapped in foil for 28 days and in water +20°C during F&T cycles (designation 28V+). [22]

The bending strengths of 28-day foil-wrapped beams are recorded in Figure 7. There is a conspicuous area of the highest bending strength. This area is also evident in the case of 28 + 30 days in foil – Figure 8. Nearly all concretes show significantly higher strengths after an additional 30 days of curing in foil.

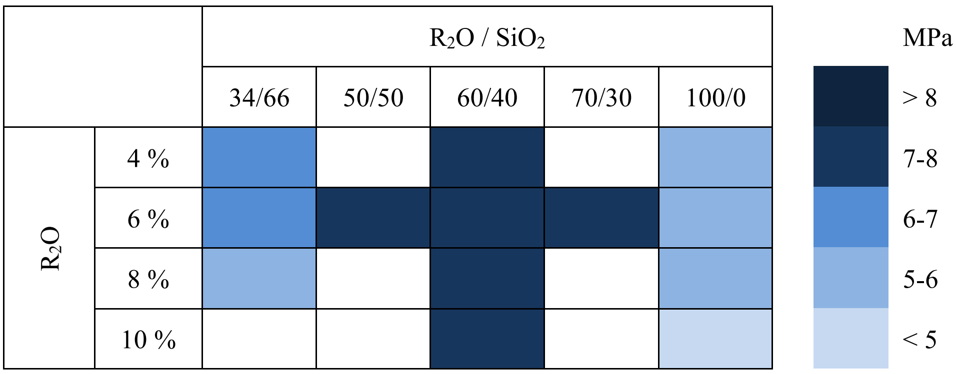

Fig. 7: Bending strengths – specimens wrapped in foil for 28 days (designation 28) [22]

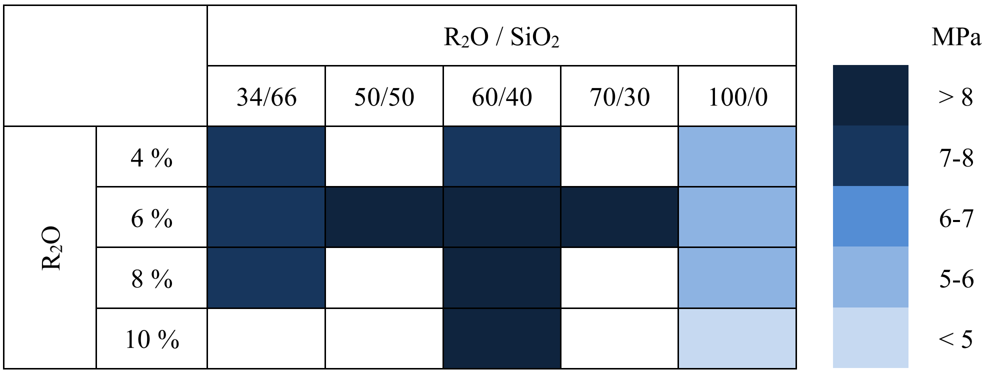

Fig. 8: Bending strengths - specimens wrapped in foil for 28 days and also in foil during F&T cycles (designation 28+). [22]

The situation is completely different in the case of the bending strength of specimens stored in water during F&T cycles, see Figure 9. All bending strengths are significantly reduced. Since some healing of (micro)-cracks is to be expected, the opposite trend was observed. This decrease in bending strengths for all mixtures after immersion of the specimens in water for 30 days is interesting and agrees with the above-mentioned results [24, 25] as well as with the role of micro-cracking and its influence on durability as reported, for example, by Wang et al. [26].

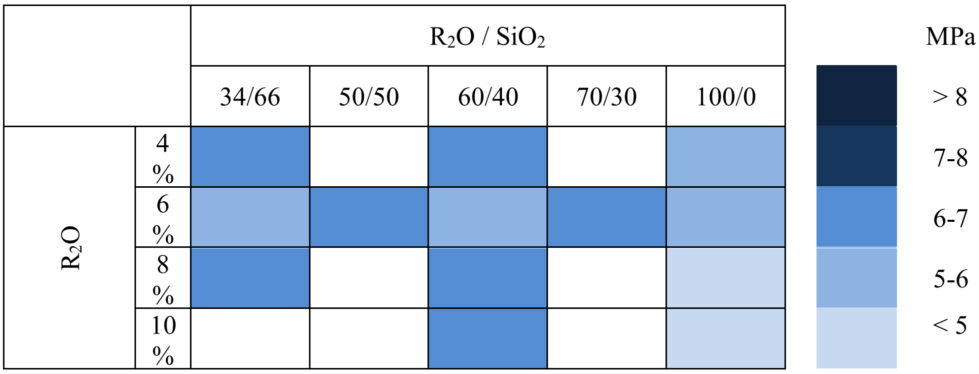

Fig. 9: Bending strengths – specimens wrapped in foil for 28 days and in water +20°C during F&T cycles (designation 28V+) [22]

2.3. Frost resistance results

As mentioned, frost resistance is evaluated by the frost resistance index, which is defined as ratio

I = properties of frosted specimens/properties of reference specimens

Compressive strengths are sometimes used as the 'properties', but more sensitive is bending strength or dynamic modulus of elasticity. It is clear from the previous section that the choice of reference specimens will be very important. Figure 10 shows a situation where the bending strength of the foil-wrapped beams at 28 days of age is taken as the reference strength. Frost resistance index is designed as I_b (b ≈ bending) in this case.

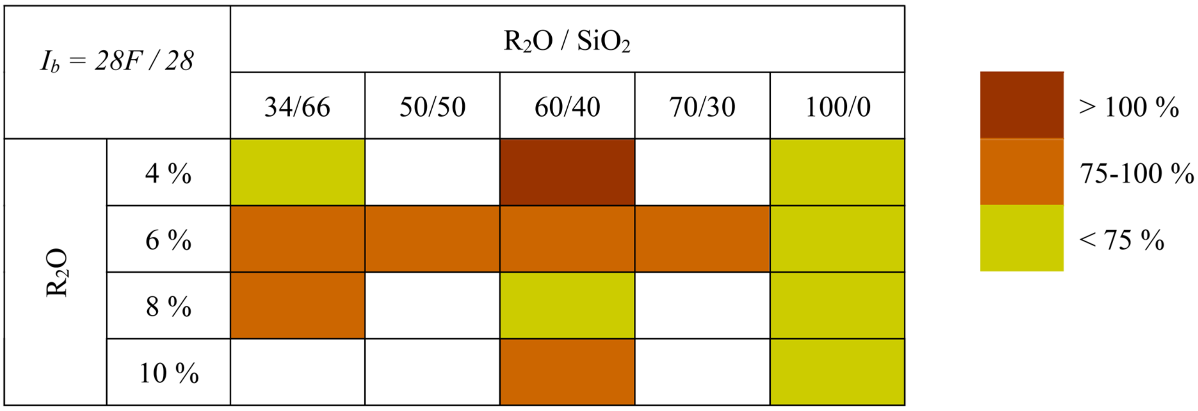

Fig. 10: Index of frost resistance I_b in terms of bending strength;
strengths of foil-wrapped beams at the age of 28 days (designation 28) are taken as reference [22]

There are concretes which show good frost resistance. One of them, R_2O = 4 %, 60/40, shows a frost resistance index higher than 100 %, which means that frosted beams show better bending strengths than reference beams. This paradox is common in high-performance concretes based on Ordinary Portland Cement.

Even better values of the frost resistance index were recorded for the reference beams placed in water at + 20°C during F&T cycles, see Figure 11. The strengths of the frosted beams are still the same as in Figure 10, but the bending strengths of additionally water-cured beams are lower than those of the foil-cured ones, see Figure 9. This means that the frost resistance index is higher. For 8 mixtures, the frost resistance index is higher than 100%, 3 mixtures are also frost-resistant and there are only 2 concretes that are not frost resistant.

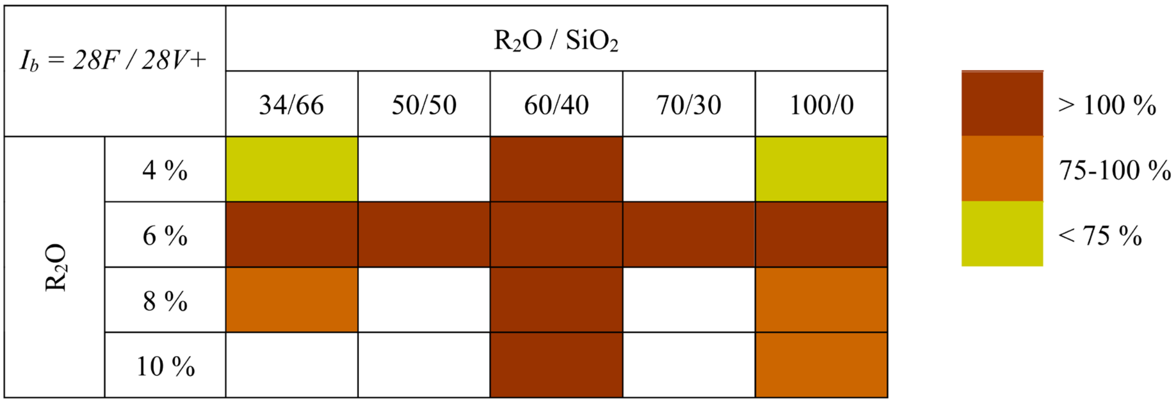

Fig. 11: Index of frost resistance I_b in terms of bending strength;
strengths of additionally water-cured beams (designation 28V+) are considered reference [22]

And finally, the situation when measuring the bending strengths of beams stored for 60 days in foil is presented in Figure 12. Only three of the 13 mixtures are frost resistant from this point of view. Again, the strengths of the frosted beams are still the same, but the strength of the reference beams is higher, see Figure 8.

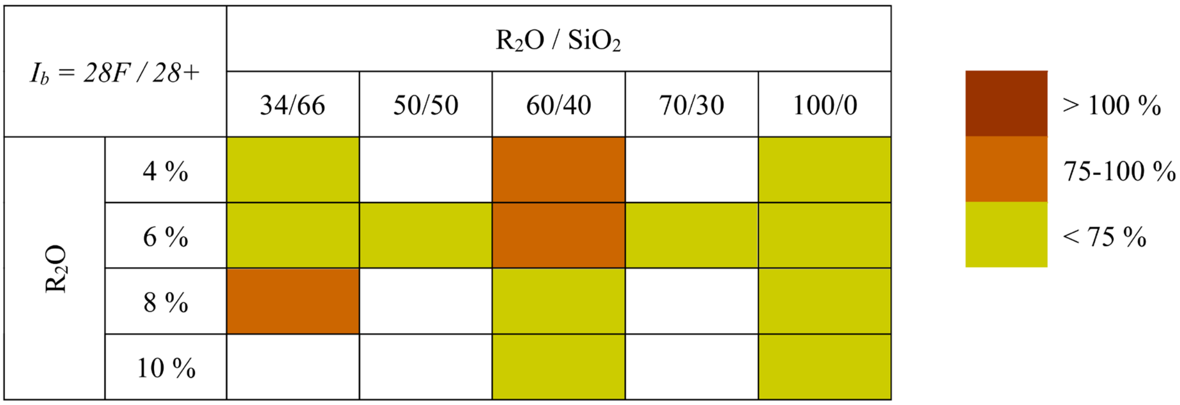

Fig. 12: Index of frost resistance I_b in terms of bending strength;
beams wrapped in foil between 28 and 60 days (designation 28+) are considered as reference. [22]

3 Conclusion

The composition of AAC in terms of R_2O and SiO_2 plays marginal role in their frost resistance. There can be found only some basic tendences – mass ratio R_2O/SiO_2 60/40 shows the best frost resistance and also 6% of R_2O is sustainable for good frost resistance. The role of w/b is not discussed in this paper.

The important finding is that the water curing of beams, that were wrapped in foil for 28 days, reduces the strength, especially the bending strength. The reason is not possible to explain from the results presented here. Some leaching of alkalis from the cured concrete may be responsible. It may also be caused by the swelling of the (R)-C-S-A-H gel, especially in the vicinity of cracks, resulting from concrete shrinkage. However, other mechanisms may also be involved. Similar, but less striking, results were also observed for ordinary Portland cement-based concretes. Curing and age of reference specimens is also very important in the case of OPC.

Based on the presented results, the frost resistance of AAM can be considered to be reasonably good when evaluated against water-cured reference specimens. However, as noted by Wang et al. [26] or Bernal and Provis [27], alkali-activated materials and ordinary Portland cement-based materials differ in reaction mechanisms, products and microstructure, and it is still questionable whether such testing methods are applicable or adequately reflect the true trends in durability. Optimization of the testing method and testing conditions seems inevitable.

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References

[1] GANDEL, R. – JERABEK, J. – MARCALIKOVA, Z.: Reinforced Concrete Beams Without Shear Reinforcement Using Fiber Reinforced Concrete and Alkali-Activated Material. Civil and Environmental Engineering, vol. 19, Iss. 1, 2023, pp. 348-356, DOI:10.2478/cee-2023-0031.

[2] KRALOVANEC, J. – MORAVCIK, Martin: Experimental Measurements in the Field of Prestressing Force Monitoring. Civil and Environmental Engineering, Vol. 18, Iss. 1, 2022, pp. 104-110. DOI: 10.2478/cee-2022-0011

[3] VAVRUS, M. – KRALOVANEC, J.: Study of Application of Fiber Reinforced Concrete in Anchorage Zone. Buildings, Vol. 13, Iss. 2, 2023, Art. No. 524. DOI: 10.3390/buildings13020524

[4] SUCHARDA, O. – MARCALIKOVA, Z. – GANDEL R. Microstructure, Shrinkage, and Mechanical Properties of Concrete with Fibers and Experiments of Reinforced Concrete Beams without Shear Reinforcement. Materials, 15 (16), art. no. 5707, 2022. DOI: 10.3390/ma15165707

[5] GÖKÇE, H.S.: Durability of slag-based alkali-activated materials: A critical review. J Aust Ceram Soc, 2024, DOI: 10.1007/s41779-024-01011-z.

[6] MATECKOVA, P. – BILEK, V. – SUCHARDA, O.: Comparative Study of High-Performance Concrete Characteristics and Loading Test of Pretensioned Experimental Beams. Crystals. Vol. 11, Iss. 4, 2021, Art. no. 427. DOI: 10.3390/cryst11040427.

[7] TU'MA, N. H. – AZIZ, M. R. – BARRY, H. J. J.: Residual Tensile Stress Estimation for Shear Strength of UHPC Nonprismatic Beams. Civil and Environmental Engineering, Vol. 17, Iss. 1, 2021, pp. 164-177, DOI: 10.2478/cee-2021-0017.
[8] MCNEIL, K. – KANG, T.H.K.: Recycled Concrete Aggregates: A Review. Int J Concr Struct Mater Vol. 7, 2013, pp. 61-69. DOI: 10.1007/s40069-013-0032-5
[9] BAKHAREV, T. J. – SANJAYAN, J. G. – Cheng, Y. B: Resistance of alkali-activated slag concrete to acid attack. Cement and Concrete Research, Vol. 33, Iss. 10, 2003, pp. 1607-1611, DOI: 10.1016/S0008-8846(03)00125-X.
[10] GLUTH, G. – GRENGG, C. – UKRAINCZYK, N. – MITTERMAYR, F. – DIETZEL, M.: Acid Resistance of Alkali-Activated Materials: Recent Advances and Research Needs. RILEM Tech Lett 2022, Vol. 7, 2022, pp. 58-67, DOI: 10.21809/rilemtechlett.2022.157.
[11] MARCALIKOVA, Z. – JERABEK, J. – GANDEL, R. – GABOR, R. – BILEK, V. – SUCHARDA, O. Mechanical Properties, Workability, and Experiments of Reinforced Composite Beams with Alternative Binder and Aggregate. Buildings Vol. 14, 2024, 2142. https://doi.org/10.3390/buildings14072142
[12] NEMEC, J., GANDEL, R., JERABEK, J., SUCHARDA, O., BILEK, V. Properties of selected alkali-activated materials for sustainable development. Civil and Environmental Engineering, Volume 20, Issue 1, June 2024,
[13] RODRIGUE, A. – DUCHESNE, J. – FOURNIER, B. – BISSONNETTE, B.: Frost Resistance of Alkali-Activated Combined Slag and Fly Ash Concrete Cured at Ambient Temperature. ACI Materials Journal, Vol. 119, Iss. 3, 2022, pp. 3-13, DOI: 10.14359/51734600.
[14] TEKLE, B.H. – HOLSCHEMACHER, K. – LÖBER, P. – HEIDEN, B.: Mechanical Behavior and Frost-Resistance of Alkali-Activated Cement Concrete with Blended Binder at Ambient Curing Condition. Buildings, Vol. 11, Iss. 2, 2021, pp. 52. DOI: 10.3390/buildings11020052.
[15] COLLEPARDI, M.: The New Concrete, Tintoretto, 2006.
[16] NEVILLE, A. M.: Properties of concrete, Harlow, Pearson Education, 12995.
[17] CYR, M. – POUHET, R.: Handbook of alkali-activated cements and concretes, 2015, doi: 10.1533/9781782422884.3.293.
[18] BILEK, V. – ZKLORZOVA, H.: Freezing and thawing resistance of alkali-activated concretes for the production of building elements, in V. M. Malhotra (Eds) Proceedings of 10th CANMET/ACI Conference on Recent Advances in Concrete Technology, Sevilla, 2009, Supplementary papers, pp. 661-675.
[19] BILEK, V. – SUCHARDA, O. – BUJDOS, D.: Frost Resistance of Alkali-Activated Concrete—An Important Pillar of Their Sustainability, Sustainability, Vol. 13, Iss. 2, 2021, art. no. 473, DOI: 10.3390/su13020473.
[20] TEKLE, B.H. - LY, T.V, HERTWIG, L. - HOLCHEMACHER, K.: Frost-resistance of Fine-Grained Alkali-Activated Cement Concrete, Structural Concrete, Vol. 24, Iss. 3, 2023, pp. 4286-4296, DOI: 10.1002/suco.202200902.
[21] BILEK, V. – PROCHAZKA, L. – MATYSKOVA, K. – SUCHARDA, O.: Frost resistance of alkali-activated concrete with different compositions, 12th ACI/RILEM International conference on cementitious materials and alternative binders for sustainable concrete, June 23 to 26, 2024 - Toulouse, France
[22] Dataset, DOI: 10.5281/zenodo.11472769
[23] BILEK, V. – OPRAVIL, T. – SOUKAL, F.: Searching for practically applicable alkali-activated concretes, 1st Int. Conf. on Advances in Chemically-Activated Materials (CAM 2010), Shi and Shen (Eds), Jinan (China) 2010, pp. 28-35, ISBN: 9782-35158-101-8.
[24] YAO, X. – YANG, T. – ZHANG, Z.: Compressive strength development and shrinkage of alkali-activated fly ash – slag blends associated with efflorescence, Materials and Structures, Vol. 49, Iss. 7, 2015, pp. 2907-2918. DOI: 10.1617/s11527-015-0694-3.
[25] CHI, M.: Effect of dosage of alkali-activated solution and curing conditions on the properties and durability of alkali-activated slag concrete, Construction of Building Materials, Vol. 35, 2012, pp. 240-245, DOI: 10.1016/j.conbuildmat.2012.04.005.
[26] WANG, A. – ZHENG, Y. – ZHANG. Z – LIU, K. – Li. Y., SHI, L. – Sun, D.: The Durability of Alkali-Activated Materials in Comparison with Ordinary Portland Cements and Concretes: A Review, Engineering, Vol. 6, Iss. 6, 2020, pp. 695-706, DOI: 10.1016/j.eng.2019.08.019.
[27] BERNAL, S. A. – PROVIS, J. L.: Durability of Alkali Activated Materials: Progress and Perspectives, J. Am. Ceram. Soc., Vol. 97, Iss. 4, 2014, pp. 997-1008. DOI: 10.1111/jace.12831.