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Olivera BUKVIĆ[1]
Antonino RUNCI[2]
Marijana SERDAR[3]

CRITICAL PARAMETERS FOR THE MIX DESIGN OF SLAG-BASED ALKALI-ACTIVATED CONCRETE

Abstract: This paper presents the results of experimental research on critical mix design parameters affecting workability and mechanical properties of alkali-activated slag-based concrete. Ground granulated blast furnace slag was used as a precursor and sodium hydroxide and sodium silicate as activators. Water to binder ratio, alkali content and silica modulus were varied as key parameters in ten alkali-activated concrete mixes. Consistency was measured by slump test and compressive strength test was performed on 150 mm cube samples. Based on the obtained results, the interdependency of critical mix design parameters and their optimal values were defined.

Key words: alkali-activated slag concrete, mix design, slump, compressive strength

KRITIČNI PARAMETRI ZA PROJEKTOVANJE SASTAVA ALKALNO-AKTIVIRANIH BETONA NA BAZI ZGURE

Rezime: U radu su prikazani rezultati eksperimentalnog istraživanja kritičnih parametara za projektovanje sastava mešavine betona koji utiču na obradljivost i mehanička svojstva alkalno-aktiviranih betona na bazi zgure. Kao prekursor, upotrebljena je granulisana zgura iz visokih peći, a kao aktivatori natrijum-hidroksid i natrijum-silikat. U deset mešavina alkalno-aktiviranog betona, varirani su vodovezivni odnos, količina alkalija i količina silicijuma u mešavini, kao ključni parametri. Konzistencija je određena merenjem sleganja, a čvrstoća pri pritisku je ispitivana na uzorcima oblika kocke, stranice 150 mm. Na osnovu dobijenih rezultata, definisana je međuzavisnost kritičnih parametara projektovanja sastava i njihove optimalne vrednosti.

Ključne reči: alkalno-aktivirani beton na bazi zgure, projektovanje sastava, sleganje, čvrstoća pri pritisku

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[1] M.Sc CE, University of Zgareb, Faculty of Civil Engineering, Department of Materials, Zagreb, Croatia, olivera.bukvic@grad.unizg.hr
[2] M.Sc, University of Zgareb, Faculty of Civil Engineering, Department of Materials, Zagreb, Croatia, antonino.runci@grad.unizg.hr
[3] Assistant Professor, PhD, University of Zgareb, Faculty of Civil Engineering, Department of Materials, Zagreb, Croatia, marijana.serdar@grad.unizg.hr

1. INTRODUCTION

Concrete is the most used construction material world-wide, and its reliability has been confirmed trough 150 years long research and structural application. However, with the annual cement production of 3.19 billion tons, the cement industry is responsible for 8% out of total CO2 emission in the world and very high consumption of natural resources [1,2]. This makes concrete unable to meet the needs of contemporary requirements for efficient, sustainable, and eco-friendly constructing. Therefore, numerous studies are steered to contribute to improvement of new types of sustainable and durable concretes made of alternative binders.

One of the possible solutions are alkali-activated materials (AAMs), based on amorphous powder aluminosilicate rich precursor and highly alkaline activator. AAMs can be generated from a wide range of aluminosilicate precursors (e.g., coal fly ash, metakaolin, different types of slags) and different activators (e.g., sodium hydroxide, potassium hydroxide, sodium silicate). Coal fly ash and metakaolin are low-calcium precursors. Due to demand for high pH, they require more alkaline solution, while slags are high-calcium precursors which can be activated by lower pH solution [3]. Since precursors are industrial by-products, not only the cement is omitted from a concrete mix, but the waste management is improved, by using waste materials in the concrete production [1]. Furthermore, research in the past decades showed that AAMs can have properties comparable to Ordinary Portland Cement (OPC) concretes, namely compressive strength, permeability, water absorption and carbonation resistance [1,4], depending on numerous factors. Although this can be promising regarding AAMs durability, further extensive research in this field has to be made to have reliable data on durability, but also on workability and mechanical properties, in order to design applicable AAMs. The type of precursor and activator, their dosage, water content, etc., influence these properties [3,5].

This paper focuses on the critical mix design parameters that will determine workability and compressive strength of concrete based on ground granulated blast furnace slag (GGBFS) as a precursor and sodium hydroxide and sodium silicate solution as activators. Experimental research of concrete based on alkali-activated concrete was performed, aiming at investigating the impact of water to binder ratio, Na_2O content and Ms on slump and compressive strength of AAC.

2. REVIEW OF CRITICAL PARAMETERS

The most important parameters affecting consistence and compressive strength are water to binder ratio (w/b), the total alkali content (i.e. Na_2O content in activator/s) and the amount of Si_2O in the activator, expressed as modulus, or silica modulus (Ms), i.e. the Si_2O and Na_2O content ratio ($Ms = n(Na_2O)/n(Si_2O)$), as well as precursor content [1,5–7]. Other important parameters are type of activator, chemical and physical properties of slag and the amount of paste in concrete [5,6], however their impact is not investigated in this paper.

Water to binder ratio (or water to solids ratio, as often referred to in the literature) is the ratio of total water to total solid in AAC. The total water is the sum of water in sodium hydroxide solution, sodium silicate, and additional water needed to achieve desired w/b ratio. Total binder is calculated as the sum of slag content, solids in sodium hydroxide solution and solids in sodium silicate solution [5,7,8]. It influences slump, as a measure of consistence, and compressive strength in AAC by the same mechanisms as in OPC concrete. Nevertheless, this is not always straightforward and it depends on alkali content and Ms as well [5].

Alkali content (n) is calculated as the sum of Na_2O in sodium hydroxide and sodium silicate solution. The alkali content increases compressive strength, due to the higher degree of alkaline activation. However, the excessive amount of alkali content can lead to efflorescence and brittleness. This content limit depends on slag type, activator and curing conditions [6]. Although there are studies reporting both lower and higher n applied in the AAC, taking into account the above stated, economic factors and the fact that for stable activation, recommended Na_2O content is 2-8%, the optimal interval of alkali content is 3-5% [5] or 3-5.5% [6]. This will also affect the optimal w/b ratio for attaining desired compressive strength. Li et al. [9] developed a model for determination of the w/b ratio and alkali content for targeted compressive strengths (**Error! Reference source not found.**). According to this research, compressive strength up to 40 MPa can be reached for 4% of Na_2O and w/b ratio in the range of 0.35-0.50. Higher compressive strengths demand higher alkali content (5%) and w/b ratio between 0.35 and 0.45. Raising alkali content up to 6% and 7% can result in compressive strengths of 60-80 MPa or higher, depending on the w/b ratio (0.35-0.50).

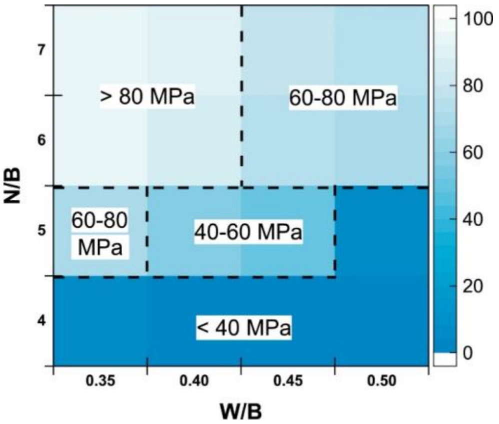


Figure 1 – Optimal w/b ratio and alkali content (N/B) for targeted compressive strength [9]

The Na_2O content also has impact on workability of the AAC mix. More liquid consistence (i.e. higher slump) can be achieved by increasing the alkali content, but its effectiveness depends on w/b ratio and Ms as well [5,6,9]. It has been reported in literature that for w/b<0.5% Na_2O content to attain S3 slump class as defined in HRN EN 12350-2 [10] is 7.5%. For w/b>0.5, the same slump class can be attained with 4% of Na_2O [5].

Modulus of the mix is calculated as the Si_2O/Na_2O ratio, where Si_2O is total silica content in the activator and Na_2O total alkali content, as stated before. Increase of Ms increases compressive strength, due to the formation of more silica gel [6]. The Ms range that provides applicable AAC is 0.6-1.5, depending on the type of slag [5,7]. For the basic slags (like GGBFS slag), the Ms will provide highest compressive strengths if in 1.0-1.5 range [5]. Higher Ms will result in lower early age compressive strengths, with later high propagation, and longer curing period needed [5]. Nevertheless, increasing Ms above 1.5 for Na_2O% below 5% could result in compressive strength decrease, due to low alkalinity of the system to achieve high degree of reactivity [5]. When Na_2O content is constant, the effect of alkali activation is constant – increase in Ms (Si_2O) will increase compressive strength. If the solids in sodium silicates are constant, higher Ms will decrease Na_2O content and the degree of alkali activation might be to low. When the alkali activation is insufficient for slag hydration, it is better to use lower Ms, otherwise, higher Ms will result in higher compressive strength [6]. It should be noted that increasing Ms and n beyond certain value, will have no effect on increasing compressive strength [7]. These values depend on slag type, activator and curing conditions [6].

Higher Ms will also result in higher slump of AAC mix [5,7]. This is more dominant for higher w/ratio, i.e. 0.55, while for lower w/b ratio, Na_2O content has more impact, according to [5]. In [5] it is also stated that for attaining S3 slump class, for w/b=0.47, Ms has to be at least 1.0. For higher w/b=0.55, S3 slump class can be attained for Ms=0.45. Some research reported that excessive increase of Ms (1.5 and higher) can result in decrease of slump, due to increased viscosity of the whole AAC mix [11].

3. EXPERIMENTAL PROGRAMME

3.1. Materials

AAC mixes were made with ground granulated blast furnace slag supplied by Ecocem Benelux as a precursor. The chemical composition from X-ray fluorescence of the slag is presented in Table 1. Sodium silicate solution (Geosil 34417 produced by Woellner) and sodium hydroxide were used as alkaline activators. The molar ratio (i.e. SiO_2(mol)/Na_2O(mol)) of Geosil sodium silicate was 1.7. Sodium hydroxide pellets were dissolved in water, making 12.5 M solution. Crushed limestone aggregate was used for the mixes, with the maximum aggregate size of 16mm.

Table 1 – Chemical composition of GGBFS

Oxide	SiO_2	Al_2O_3	CaO	Fe_2O_3	MnO	TiO_2	MgO	K_2O	Na_2O	SO_3
Wt% of GGBFS	31.1	13.7	40.9	0.401	0.31	1.26	9.16	0.685	0	2.31

3.2. Mix design

Ten AAC mixes were prepared, in order to determine the optimal intervals of critical parameters affecting slump and compressive strength, for the given type of GGBFS. The mix proportion was calculated based on absolute volume of 1m^3 of the AAC mix, with constant slag content of 375 kg/m^3 for each mix and different w/b ratios. The total amount of water was calculated as the sum of water from activators and extra fresh water added. The total amount of solids in w/b ratio represents the sum of slag, sodium hydroxide and sodium silicate pellets. The alkali content was calculated as the sum of Na2O in sodium hydroxide and sodium silicate, expressed as weight percent of ground granulated blast furnace slag (wt% GGBFS). Ten mix designs were studied and reported in Table 2. Four mix designs were based on the RILEM Round Robin test mix SN3 [8], with modified w/b ratio (MS1 and MS2) or with modification of w/b ratio along with Na_2O content and Ms (MS3 and MS4). In other mixes, these parameters values were chosen as potential thresholds regarding slump and compressive strength, based on literature [7]. MS5, MS6 and MS7 mixes with w/b=0.42 were designed aiming to test the impact of varying Ms from 0.42 to 1.03 coupled with Na_2O content below and over 4%. Furthermore, mixes MS8, MS9 and MS10 had constant w/b=0.45, as well as Ms=1.03, but different Na_2O content – from 3,5%-5%, aiming to investigate the effect of >4% with Ms>=1 and higher w/b=0.45. The aggregate grading curve was defined according to the EMPA curve, with fine to coarse aggregate ratio 1:1.5 for each mix.

Table 2 – Mix design and results of slump and compressive strength testing of AAC mixes

Mix	**GGBFS [kg/m^3]**	**w/s**	**Na_2O***	**SiO_2***	**Ms**	**Slump [mm]**	**Slump class****	**fc(2d)**	**fc(7d)**	**fc(28d)**
MS1	375	0.44	3.5	0.7	0.22	130	S3	16.66	26.8	38.32
MS2	375	0.39	3.5	0.7	0.22	10	S1	26.09	39.42	56.92
MS3	375	0.44	2.5	0.4	0.15	30	S1	15.41	23.89	33.31
MS4	375	0.47	2.5	0.4	0.15	50	S2	13.83	22.2	32.49
MS5	375	0.42	4.1	1.7	0.42	55	S2	34.05	47.49	-
MS6	375	0.42	2.8	1.9	0.69	78	S2	24.4	50.13	-
MS7	375	0.42	4.3	4.3	1.03	75	S2	41.83	37.51	-
MS8	375	0.45	3.5	3.5	1.03	120	S3	26.28	57.98	-
MS9	375	0.45	4.3	4.3	1.03	157	S3	35.17	63.84	-
MS10	375	0.45	5.0	5.5	1.14	212	S4	42.86	65.9	-

*wt% GGBFS
**In accordance with [10]

3.3. Sample casting and curing

The mixing was conducted according to the following procedure. Aggregates and GGBFS were mixed for 1 minute. After that, sodium silicate and sodium hydroxide were continuously added, respectively, and mixed for 2 minutes. Water was added next and mixed for 4 minutes. For each mix, three 150 mm cube samples were casted, after performing testing of fresh properties of AAC. Following the casting, the samples were covered with plastic sheets to avoid excessive drying of the top surface. After 24h, samples were demolded, wrapped in polymeric films to prevent moisture loss, and stored in curing chamber until compressive strength testing.

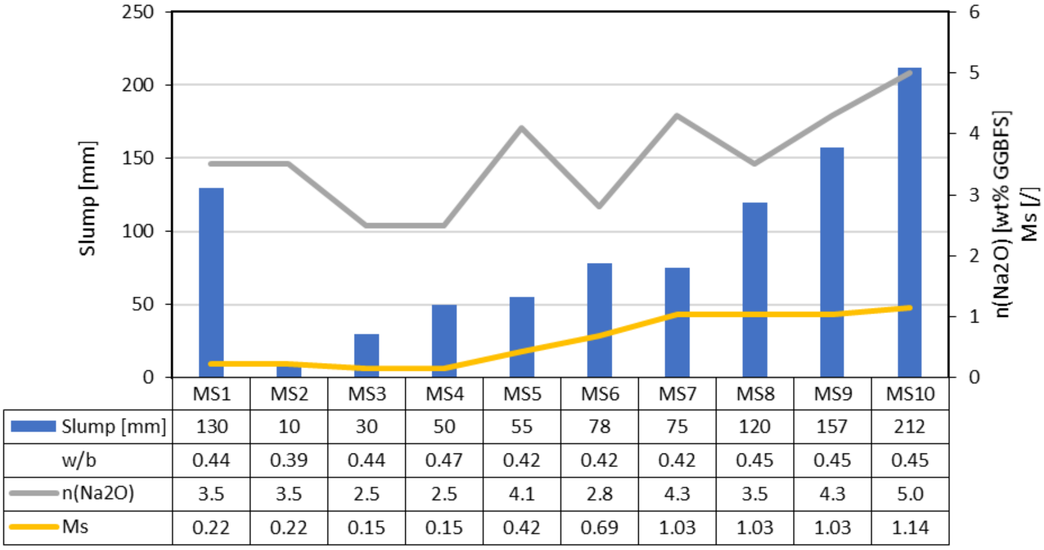
3.4. Test methods

The consistence of fresh concrete was measured by slump test in accordance with HRN EN 12350-2 [10]. The compressive strength was tested according to HRN EN 12390-3 [12] at 2, 7 and 28 days, using universal testing machine.

4. RESULTS

4.1. Slump test

The results of slump test are shown in Figure 2 and Table 2. Based on the presented results, when varying n and Ms, w/b ratio affects the AAC mix slump the same the same way as the OPC concrete mix slump, only up to certain values of w/b ratio, Na_2O content and Ms. Mix MS2 has the lowest w/b ratio and lowest slump, while mix MS1 has the highest slump, but not the highest w/b ratio. This can be explained by higher amount of Na_2O, which is in accordance with the data reported in literature [5,11]. Nevertheless, increasing the Na_2O content in mix MS2 did not have the effect on slump due to low w/b ratio (i.e., 0.39). Higher w/b ratio in mixes MS2 and MS3 resulted only in slight increase in slump due to the lower Na_2O content in these mixes. However, mix MS1 had significantly higher slump among these four mixes, even though w/b ratio was the same as the MS3 and lower than in mix MS4. Therefore, increased Na_2O content has higher impact on slump than increasing w/b ratio, for w/b>0.39.



	MS1	MS2	MS3	MS4	MS5	MS6	MS7	MS8	MS9	MS10
■ Slump [mm]	130	10	30	50	55	78	75	120	157	212
w/b	0.44	0.39	0.44	0.47	0.42	0.42	0.42	0.45	0.45	0.45
▬ n(Na2O)	3.5	3.5	2.5	2.5	4.1	2.8	4.3	3.5	4.3	5.0
▬ Ms	0.22	0.22	0.15	0.15	0.42	0.69	1.03	1.03	1.03	1.14

Figure 2 – Slump values of AAC mixes

Mixes MS5, MS6 and MS7 attained slightly higher slump values than mixes MS2, MS3 and MS4, with lower w/b ratio, by increased Na_2O content above 4% and also by increasing Ms. It should be noted that the Ms had significant impact on slump when comparing MS6 (n=2.8%) to mixes MS2, MS3 and MS4, but not when comparing MS5, MS6 and MS7 which had the same w/b=0.42.

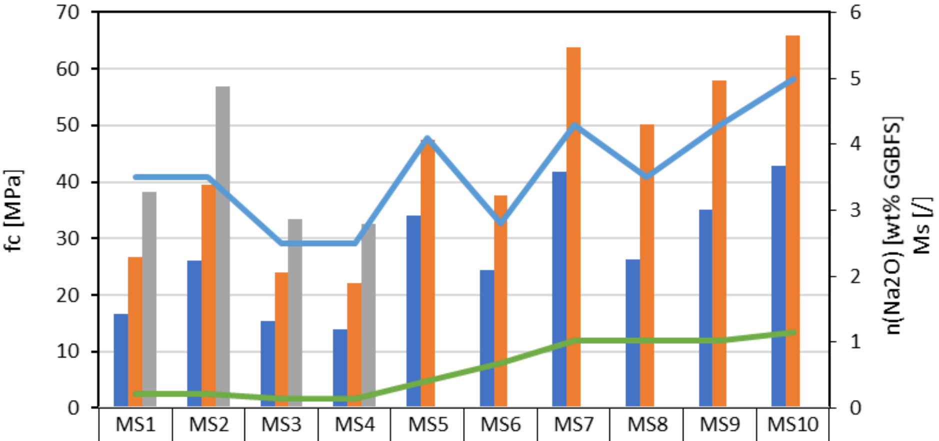
Therefore, it can be concluded that increasing Ms is affecting slump for higher w/b ratios, confirming the literature statements [5].

By analyzing previously mentioned parameters in mixes MS8, MS9 and MS10 which had the same w/b ratio=0.45, it is clear that increasing Na_2O content to 3.5% and Ms to 1.0 or higher resulted in higher slump values. S3 slump class could be attained for n=3.5% or higher (mixes MS8 and MS9), while further increase of n and Ms resulted in slump class S4 (mix MS10).

4.2. Compressive strength test

The results of the compressive strength tests at 2, 7 (mixes M1-MS10) and 28 days (mixes MS1-MS4) are shown in Figure 3 and Table 2.

Lowering the w/b ratio resulted in higher compressive strengths at 2, 7 and 28 days, as expected. When comparing the same or similar w/b ratios, the compressive strength increases with Na_2O content, due the higher reaction degree and C-A-S-H gel precipitation in the matrix [5,13]. This will have dominant effect on compressive strength comparing to w/b ratio, for Na_2O=4% or higher, as shown by compressive strengths at 7 days of the mixes MS5, MS7, MS8, MS9 and MS10. The progression of compressive strength is also affected by increase of Ms, since it is highly proportional to SiO_2 content. If the Ms is lower than 1.0, Na_2O content will still have the dominant effect on strength. However, after reaching the value of 1.0, Ms has more impact. This can be concluded following the results of 7 days compressive strength of mixes MS5-MS10. For the same w/b ratio, lower n, and higher Ms than mix MS5 (but still under 1.0), mix MS6 has lower 7 days compressive strength than the mix MS5, with the difference of 10 MPa. Mixes MS6 and MS7 had similar n (higher than 4%), the same w/b ratio, but the Ms of the mix MS7 was higher and reached the value of 1.0. This led to MS7 7-day compressive strength increase for 17MPa, compared to MS6. Furthermore, even for increased w/b ratio in mixes MS8-MS10, 7-day compressive strength is higher than for mixes MS5-MS7, although it is significant increase only compared to mix MS6 where the n is lower than 4%.



	MS1	MS2	MS3	MS4	MS5	MS6	MS7	MS8	MS9	MS10
🟦 fc (2d)	16.66	26.09	15.41	13.83	34.05	24.4	41.83	26.28	35.17	42.86
🟧 fc (7d)	26.8	39.42	23.89	22.2	47.49	37.51	63.84	50.13	57.98	65.9
⬜ fc (28d)	38.32	56.92	33.31	32.49						
w/b	0.44	0.39	0.44	0.47	0.42	0.42	0.42	0.45	0.45	0.45
— n(Na2O)	3.5	3.5	2.5	2.5	4.1	2.8	4.3	3.5	4.3	5.0
— Ms	0.22	0.22	0.15	0.15	0.42	0.69	1.03	1.03	1.03	1.14

Figure 3 – Results of 2, 7 and 28 days compressive strength test of AAC mixes

However, further increase in 28-day compressive strength of mixes MS7-MS10 is expected, since mixes with higher Ms result in lower early age strength, and higher strengths after 28 days [5,6], which can be expected to be 80-90% of 91-day strength, according to [5]. The later high propagation of compressive strength can already be confirmed on mixes MS7-MS10, where difference between 2 and 7-days compressive strength the difference between 2-days and 7-day compressive strength is 22-26 MPa. For the mixes with lower Ms, this difference is 10-14MPa.

5. CONCLUSIONS

The experimental research presented in this paiper aimed for investigating the effect of critical parameters for attaining targeted slump and compressive strenght of AACs. Analyzing the results obtained by varying w/b ratio, Na_2O content and Ms, the following can be concluded:

- Na_2O content higher than 4 wt% GGBFS impacts slump increase more significantly than increasing w/b ratio;
- Higher Ms increases slump value. This effect is more expressed for Ms>1.0 or higher w/b ratios;
- S3 slump class can be attained even for lower Na_2O content (i.e.,3.5%) and Ms=1.0, for w/b=0.45;
- Na_2O content higher than 3.5 wt% GGBFS increases compressive strenght;
- Higher Ms increases compressive strenght for Na_2O content higher than 3%. This effect is conspicious for Ms>1.0.
- 28-day compressive strenght up to 38 MPa with the satisfactory workability of the mix can be achieved for Na_2O content 3.5%, Ms=0.22 and w/b ratio 0.44;
- Ms>=1.0 results in lower early age (i.e. 2 days) compressive strengths, with an increase at 7 days up to cca 50%.
- 7-day compressive strenght higher than 40MPa can be attained even for lower Na_2O content (i.e.,4%) and Ms=0.42, for w/b ratio 0.42. Further increase in Na_2O content up to 5% and Ms value up to 1.14 will increase 7-day compressive strength up to 65MPa, even for w/b ratio 0.45.

From ten mix designs presented in this paper, three will be chosen for further experimental research on durabiliity of AAC under combined environmental actions.

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