**JOURNAL OF THE SERBIAN CHEMICAL SOCIETY**

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Dear Editor,

Please find our revised manuscript “***Durability of alkali activated slag in a marine
environment: influence of alkali ion*”.** We wish to submit the revised manuscript for consideration of publication in ***Journal of Serbian Chemical Society***.

Following your suggestions, we have carefully considered the comments provided by the reviewer and modified our manuscript to address their concerns. We have clarified a number of issues in the text and believe that the revised manuscript is much better as a result of changes. We appreciate the reviewer’s comments and aid in making this a better paper. We have included a detailed response to the referee’s comments below.

We look forward to receiving your comments and thank you for consideration of this manuscript.

Sincerely,

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**REPILES TO THE REFEREE’S COMMENTS - (A)**

**The main objective of the paper was to evaluate influence of the alkaline activator on the properties of alkali activated slag (durability in marine environment). Paper is clear and well-written. However, few important parts are missing. First, more detailed discussion on the influence of the different activator on the properties of the resulting alkali activated material (e.g. explanation for the lower porosity of Na-based alkali activated slag). Then, detailed description of the experimental procedure used for testing durability of alkali activated slag is missing, as well as comparison of the obtained data with data / results from the literature.**

Response:

We are very much thankful to the reviewer ″A″ for his/her deep and thorough review. We have revised our paper in the light of reviewer′s useful suggestions and comments. We made an effort to improve the paper by evaluation of influence of the different activator on the properties of the resulting alkali activated material. Special attention is given on the influence of alkali ion ( Na or K) on the properties of AAS samples, we provided a more detailed description of experimental procedure and we compared our results with the literature data.

**Some specific comments follow:**

1. **Line 17: ...exposed to**
* The correction is made. (please refer to page 1)
1. **Line 46: Instead of “calcium (alumina) silicate hydrate”, perhaps it`s better to use “aluminium-containing calcium silicate hydrate” or “calcium aluminosilicate hydrate”**
* The correction is made. We used the term "*aluminium-containing calcium silicate hydrate".* (please refer to page 2)

1. **Lines 51-52: “... the C-S-H phases which exist in the hydration product of OPC”.** **C-S-H is the main hydration product of OPC, rephrase.**
* The correction is made ( please refer the page 2)
1. **Lines 82-83: For the purpose of alkali activation EAFS was grinded... Better: Prior to alkali activation..**
* The correction is made. (please refer to page 4)
1. **Lines 94-95: Samples were “left to rest 14 days at ambient temperature before any testing”. What were the temperature / humidity of the ambient?**
* The data in regards to the temperature/humidity of ambient were provided. The AAS samples were left to rest 14 days in a laboratory room at the temperature of 22 ± 2°C and 35 % relative humidity before any testing was performed. This explanation is included in *Experimental* section. (please refer to page 4)
1. **Lines 95-96: Were the samples exposed to seawater in real conditions (immersed in sea)? Or, how was the solution of seawater prepared? What was the volume of the solution and what was solution / samples mass ratio? What was the temperature of the solution? Scientific literature is relatively
abundant with results showing good resistance of alkali activated materials to various aggressive solutions; however, the need for unique / standard testing procedures has been recognized long time ago.**
* Durability of Na-AAS and K-AAS was tested by immersing the samples in seawater for a period of 14 weeks. For this purpose, two groups of five AAS samples of same series (Na- or K-AAS) were exposed to seawater attack. Natural seawater (pH 8.3) was taken for experiment. Prior to the experiment, seawater was poured into polyethylene flasks and left to stay for a period of 7 days to reach the temperature of laboratory room. The volume of seawater was 2 dm3 per five samples of same series. The volume of each sample was approximately 0.03 dm3. This explanation is given in the *Experimental* section. (please refer the page 4)
1. **Table II. Please, add details on compressive strength measurement in the Experimental section.**
* We agree with the reviewer’s suggestion that details on compressive strength measurements should be added. We made appropriate changes in the manuscript. Five control AAS samples of each series were tested for compressive strength on an HP-400 hydraulic press at room temperature in air (standard test conditions). Before testing, the surfaces of the sample were polished flat and parallel. Compressive strength measurements were performed according to the MEST EN 1354:2011 standard using five cylinders of each series and averaging the obtained experimental values. This explanation is included in the *Experimental* part of manuscript. (please refer to page 4 and 5)
1. **Line 144: Un-reacted slag particle is marked as B in Figure 2, and reaction products as A.**
* We thank the reviewer for pointing out this oversight. This was an error and we have made the corrections in Fig 2. (please refer to page 9)
1. **Lines 145-149: Are the EDS results given in Table III based on single or multiple point analysis? If multiple, how many points were analysed?**
* The EDS results (Table III) provided in the initially submitted version of manuscript were based on single point analysis. The data in table III are corrected, taking into account the similar suggestion of both reviewers. The EDS data presented in revised version of manuscript were obtained from the average of three sample areas (free of slag). The values of standard deviation in Table III were also provided. (please refer to page 9)
1. **Lines 149-151: What would be a possible explanation for lower porosity, higher strength and lower Ca/Si ratio in reaction products of sodium silicate activated slag? What is the advantage of sodium silicate as an alkaline activator, compared to potassium silicate? pH of the solution, ionic radius of the cation, different distribution of silicate polymeric species in the solution...?**

* We thank the reviewer for this very useful suggestion. We made an effort to improve the paper by evaluating the influence of alkali ion on the properties of AAS samples.

(Please refer to pages 6 and 7.)

This additional evaluation of results of investigation is accompanied by the new references:

25. M. Salman, Ö. Cizer, Y. Pontikes, R. Snellings, L. Vandewalle, B. Blanpain, K. Van Balen, *J. Hazard. Mater.* **286** (2015) 211–219 (http://dx.doi.org/10.1016/j.jhazmat.2014.12.046).

26. A. Dakhane, Z. Peng, R. Marzke, N. Neithalath, *Adv. Civ. Eng. Mater.* **3** (2014) 371–387, (http://dx.doi.org/https://doi.org/10.1520/ACEM20140005.).

27. J. H. Sharp, E. M. Gartner, D. E. Macphee, *Adv. Cem. Res.* **22** (2010) 195–202 (http://dx.doi.org/10.1680/adcr.2010.22.4.195).

28. P. Steins, A. Poulesquen, O. Diat, F. Frizon, *Langmuir* **28** (2012) 8502–8510 (http://dx.doi.org/10.1021/la300868v).

29. W. M. Kriven, J. L. Bell, M. Gordon, *Microstructure and Nanoporosity of as‐Set Geopolymers*, in R. Tandon, A. Wereszczak, E. Lara‐Curzio (Eds.), *Mech. Prop. Perform. Eng. Ceram. II Ceram. Eng. Sci. Proc.*, John Wiley & Sons, New Jersey, 2006, pp. 491–498.

31. I. Nikolić, A. Drinčić, D. Djurović, L. Karanović, V.V. Radmilović, V.R. Radmilović, Constr. Build. Mater. 108 (2016) 1–9 (http://dx.doi.org/10.1016/j.conbuildmat.2016.01.038).

1. **Line 169: What was the starting pH of seawater solution?**
* The initial value of pH for seawater prior to immersion of specimens was 8.3. (Please refer to page 4).
1. **Line 173: What was the thickness of brucite protective layer? Was there a difference in the thickness of the protective layer formed on Na-AAS sample compared to K-AAS sample?**
* The thickness of protective layer formed on the surface of AAS samples was not measured. Namely, the erosion of protective layers was observed during the continual inspection of surfaces samples within 14 weeks. Thus, the thicknesses of protective layers were not relevant and were not measured. Only the inspection of near surface region for both samples was done.
1. **Lines 217-220: What would be possible explanation for easier penetration of Cl- ions through the protective layer of K-AAS?**
* This could be attributed to the crystallinity of the protective layer formed on the surface of the AAS samples, but this view requires more detailed research. As shown by XRD analysis (Figure 5), the protective layer on the surface of the sample K-AAS was less crystalline than that formed on the surface layer of N-AAS. (please refer to page 12)
1. **References: Puertas F.et. al. (Alkaline cement mortars: chemical resistance to sulfate and seawater attack, Materiales de Construccion, 52 (267), 55–71, 2002) also investigated durability of alkali activated slag in seawater. Perhaps it would be interesting to compare results presented in this paper with results obtained by Puertas et. al.**
* As suggested by the reviewer, we have added the additional reference (Ref. 22. in the revised version of manuscript) to compare our results with the literature data. Please refer the section *Durability of AAS samples* in the revised manuscript. (please refer to pages 10).

Moreover, according to the suggestion by reviewer B, we also used this reference to provide the more detailed evaluation of durability of AAS in seawater. Please refer to section *Introduction.* (please refer to page 3)

New references added:

22. F. Puertas, R. De Gutiérrez, A. Fernandez-Jimenez, S. Delvasto, J. Maldonado, Mater. Construcción 52 (2002) 55–71 (http://dx.doi.org/https://doi.org/10.3989/mc.2002.v52.i267.326).

23. H. El-Didamony, A.A. Amer, H. Abd Ela-Ziz, Ceram. Int. 38 (2012) 3773–3780 (http://dx.doi.org/10.1016/j.ceramint.2012.01.024).

**REPILES TO THE REFEREE’S COMMENTS - (B)**

 **Overall comments**

 **This paper explored the influence of different alkali activators (or alkali ions) on resistance of alkali-activated steel electric arc furnace slag to external seawater attack. The paper is interesting and suitable for the Journal of the Serbian Chemical Society. However, paper also possesses some shortcomings. Specific comments are given bellow.**

1. **INTRODUCTION

“Durability of AAS in aggressive environments is the main advantage of these materials over OPC and thus the behavior of AAS in а marine environment is of great importance due to the presence of variety of harmful spieces.” The durability of AAS in aggressive environments is insufficiently described, particularly the resistance to seawater attack. For example have a look at F. Puertas, R. de Gutierrez, A. Fernandez-Jimenez, S. Delvasto, J. Maldonado, Alkaline cement mortars. Chemical resistance to sulphate and seawater attack, Materiales de Construccion 52  (2002) 55–71 or H. El-Didamony, A.A. Amer, H. Abd-El-Aziz, Properties and durability of alkali-activated slag pastes immersed in seawater, Ceramics International 38 (2012) 3773–3780.**
* The authors gratefully thank to reviewer for this useful suggestion. As suggested, literature review is updated substantially with new references. We hope that important evaluation of durability of AAS in seawater is improved in this paper by the evaluation of additional references:

22. F. Puertas, R. De Gutiérrez, A. Fernandez-Jimenez, S. Delvasto, J. Maldonado, Mater. Construcción 52 (2002) 55–71. (http://dx.doi.org/https://doi.org/10.3989/mc.2002.v52.i267.326).

23. H. El-Didamony, A.A. Amer, H. Abd Ela-Ziz, Ceram. Int. 38 (2012) 3773–3780 (http://dx.doi.org/10.1016/j.ceramint.2012.01.024).

Please refer to page 3.

**EXPERIMENTAL:**

1. **Mixture of NaOH and Na2SiO3 solutions is still a sodium silicate solution, but of different SiO2/Na2O molar or mass ratio. It is more appropriate to describe the sodium silicate solution by its SiO2/Na2O ratio. Furthermore, the concentration of sodium silicate solution is usually expressed as % of Na2O in respect to the dry mass of solid precursor(s). For more information, have a look at ref. 12. Similar situation is in the case of potassium silicate. This issue should be further clarified.**
* We appreciate this and agree with the reviewer’s suggestion. We made an appropriate change accordingly. Na-activator was prepared by mixing 10 M NaOH and liquid Na2SiO3 (SiO2/Na2O molar ratio of 3.2), while the K-activator was prepared by mixing 10 M KOH and liquid K2SiO3 (SiO2/Na2O molar ratio of 3.2) solutions. Accordingly, Na- activator was added as 4.8 % and 4.8 % by mass of Na2O and SiO2, respectively while K- activator was added as 7.6 % and 4.4 by mass of K2O and SiO2, respectively. (Please refer to page 4).

The K-activator contained a slightly higher amount of K2O (7.2 by mass K2O) than the corresponding amount of Na2O in the Na-Activator (4.8% Na2O), so that the loss of strength induced by replacing the Na- with the K-activator would be greater than in the case of the same amount of Na2O and K2O in the corresponding activator. This was not explored in detail at this time but may be of interest in future research. (Please refer the page 6).

1. **“The paste obtained by alkali activation was cast in a plastic cylindric mold (28** × **60 mm) and cured for 48 h at 65 °C. Subsequently, the AAS samples were removed from molds and left to rest 14 days at ambient temperature before any testing was performed.” Curing at elevated temperature (open or closed/covered?) should be clarified. Relative humidity during curing at ambient temperature should also be clarified.**
* The paste obtained by alkali activation was cast in a plastic cylindric mold (28 × 60 mm), sealed with a lid to prevent the loss of evaporating water and cured for 48 h at 65 °C. Subsequently, the AAS samples were removed from molds and left to rest 14 days in a laboratory room at the temperature of 22 ± 2°C and 35 % relative humidity before any testing was performed. Please refer the *Experimental* section. (Please refer to page 4)
1. **The seawater resistance testing, which is the most important part of experimental work, should be described more in details.**
* We thank the reviewer for this very useful suggestion. We made an effort to improve the paper by more detailed explanation of seawater resistance testing, taking into account similar suggestion by reviewer A (comment No 6). (Please refer to *Experimental section,* page 4)

 **RESULTS AND DISCUSSION**

1. **Characterization of AAS samples. The XRD Powder Diffraction Files (PDF) for the crystalline phases identified should also be given. The main product(s) of alkali activation of slag, such as C-S-H or C-A-S-H gel, was not identified in the AAS samples (Fig. 1)?**
* The JCPDS were provided for crystalline phases (section *Characterization of AAS samples*). No crystalline C-A-S-H phase was detected by XRD since the reaction product of slag alkali activation exhibits an amorphous structure in XRD. (please refer to page 7).

 The C-(A)-S-H gel, with a high content of alkali ions (Na+ or K+), as the main reaction product in the alkali activation process is detected by SEM/EDS analysis. (please refer page 9)

Moreover, the sentence in the *Introduction* section

…. The structure of C–(A)–S–H gel is similar to the C–S–H structure in OPC, although it is highly amorphous and characterized by a high aluminum content, indicating a high degree of aluminum substitution for silicon in bridging positions.14....

was slightly corrected to:

*.....The structure of C–(A)–S–H gel is similar to the C–S–H structure in OPC, although it is highly* ***amorphous*** *and characterized by a high aluminum content, indicating a high degree of aluminum substitution for silicon in bridging positions*.*14*

 Please refer to page 2.

1. **How many EDS analyses were performed (data given in Table III)? If these data are based on a single point analysis Table III should be omitted from the manuscript. If meaningful number of analysis was performed then standard deviation should be given as well.**
* The EDS results (Table III), provided in initially submitted version of manuscript, were based on single point analysis. The data in table III are corrected taking into account the similar suggestion of both reviewers. The EDS data presented in revised version of manuscript were obtained from the average of three sample areas. The values of standard deviation in Table III were also provided (Please refer to page 9)
1. **Durability of AAS samples. The exact compressive strength data after seawater attack are not given. All compressive strength data should be accompanied with standard deviations.**
* We provided the data of compressive strength of samples before and after the seawater attack, accompanied with the standard deviation. The values of compressive strength and standard deviation for both samples before durability test are given in the Table II (please refer to page 7)

The strength of Na- and K-AAS samples after seawater attack were 37.8±0.8 MPa and 28.8±1.1 MPa, respectively.

Please refer to page 9.

1. **The discussion is weak. The results of the seawater resistance testing should be compared with other published data, which should also be explored more in details in the Introduction section, as previously mentioned.**
* We thank both reviewers for bringing this point to our attention. We made an effort to improve the paper by more detailed evaluation of literature data with regards the AAS resistance in seawater (please refer section *Introduction,* page3). We take into account the suggested references:

22. F. Puertas, R. De Gutiérrez, A. Fernandez-Jimenez, S. Delvasto, J. Maldonado, Mater. Construcción 52 (2002) 55–71 (http://dx.doi.org/https://doi.org/10.3989/mc.2002.v52.i267.326).

23. H. El-Didamony, A.A. Amer, H. Abd Ela-Ziz, Ceram. Int. 38 (2012) 3773–3780 (http://dx.doi.org/10.1016/j.ceramint.2012.01.024).

We also compared our results with the results reported by Puertas et al. (section *Durability of AAS samples,* page 10).

However, the results could not be compared with the results reported by El-Didamony et al. due to the different methodology of AAS sample preparation. Namely, El-Didamony et al. investigated the seawater resistance of AAS sample, but the AAS samples were prepared using the seawater, which was not the case in our study. We prepared our samples with the distilled water.

1. **Sorptivity of AAS samples. The capillary sorptivity coefficient SI unit does not seem to be correct?**
* We thank the reviewer for pointing out the typing error and we made the correction. The capillary sorptivity coefficient unit is kg m-2 s-1/2. (Please refer to page 14)