Dear Editor Icy Liu and Reviewers:

Thank you for your letter and for the reviewers’ comments concerning our manuscript entitled “Study on the Preparation and Performance of Alkali-activated Coal Gangue-Slag Cementitious Materials” (Manuscript number: materials-533306). Those comments are all valuable and very helpful for revising and improving our paper, as well as the important guiding significance to our researches. We have studied comments carefully and have made corrections which we hope meet with approval. Revised portions are marked in red in the manuscript. The main corrections in the manuscript and the responses to the reviewer’s comments are as following:

Responds to the reviewer’s comments:

Reviewer #1:

Thanks to Reviewer for their affirmation and suggestion of the manuscript. Moreover, we are very sorry for the difficulties our writing has brought to the reviewers. We revised it according to your suggestions and replied to your questions. In the introduction section, we highlight the research background and significance, and supplement the references related to the research content of this paper. We have supplemented the experimental process and curing conditions, and we have also proofread and polished the conclusion, making the study of this manuscript more meaningful. Other modifications details are marked in red in the manuscript. Thank you for your time and recognition. I look forward to the opportunity to discuss academic...
1. Response to comment: Please add the element for which MAS-NMR testing was done.

Response: Thank you for your suggestion, and your suggestion is also very important. According to the opinions of reviewers, the MAS-NMR in the abstract was modified to $^{29}$Si MAS-NMR, which was marked red in the manuscript.

2. Response to comment: Introduction has to be enriched with other references related to the performed research of authors.

Response: Thank you for your suggestion, and your suggestion is also very important. According to the opinions of reviewers, we expanded the research background in the introduction section, and added references related to the research content, highlighting the research significance, and modifying the manuscript to make it more substantial and meaningful. Specific modifications are marked in red in the manuscript.

3. Response to comment: What is the Sulfur content of slags? Please, report the contents of S.

Response: We are very sorry for our negligence. Since the content of SO$_3$ in calcined gangue is only 0.03%, the content of SO$_3$ is not marked in Table 1. According to the opinions of reviewers, Table 1 has been improved. The corresponding modifications are marked in red in the manuscript.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Calcined coal gangue</th>
<th>Slag</th>
<th>Cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>56.56</td>
<td>30.58</td>
<td>20.88</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>36.78</td>
<td>14.04</td>
<td>5.57</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td>-----</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>CaO</td>
<td>0.62</td>
<td>38.43</td>
<td>62.09</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.95</td>
<td>0.35</td>
<td>2.40</td>
</tr>
<tr>
<td>MgO</td>
<td>0.22</td>
<td>10.57</td>
<td>2.43</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.42</td>
<td>0.57</td>
<td>0.32</td>
</tr>
<tr>
<td>SO₃</td>
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<tr>
<td>TiO₂</td>
<td>2.10</td>
<td>1.93</td>
<td>0.31</td>
</tr>
<tr>
<td>LOI</td>
<td>1.32</td>
<td>1.17</td>
<td>0.98</td>
</tr>
</tbody>
</table>

4. **Response to comment**: Why LOI is so high for slag (3.53)?

**Response**: According to the opinions of the reviewers, we retested the LOI of slag, and found that the LOI of the slag was 1.17%. According to the references, the LOI of slag is about 1.0-1.50, and the LOI meets the requirements after redetermination. The corresponding modification are marked in red in the manuscript.

5. **Response to comment**: Please, add particle size distribution and chemical composition of your Cement P.O 42.5.

**Response**: Thank you for your suggestion. Our research group determined the chemical composition of cement, as shown in Table 2 above. The corresponding modification are marked in red in the manuscript.

Regarding the particle size distribution curve of P.O. 42.5 cement, I would like to give two explanations:

(1) The main research materials in this manuscript are coal gangue and slag, and P.O. 42.5 cement is only tested for one group, which serves as the control experiment to prove that the strength of AACGS paste is feasible. If the particle size distribution curve of P.O.42.5 cement is added in the manuscript, the reader will think that P.O.42.5 cement is also the key material of this manuscript.
Different from coal gangue powder and slag, the production of cement is standard industrial production, and the fineness and chemical composition of cement produced in different regions are not much different. So the size distribution of cement is given, which is of no value to readers in subsequent research. On the contrary, the chemical composition and particle size distribution of coal gangue and slag processed and produced in different regions and factories are quite different. It is important to give the particle size distribution of coal gangue and slag in the manuscript.

6. Response to comment: Table 4 What is macrography tests? What is microcosmic tests? What is cosmic? Why macrography?

Response: In terms of manuscript test experiment, macrography tests includes paste fluidity, compressive strength and non-evaporative water content; microcosmic tests includes XRD, FT-IR, $^{29}$Si MAS-NMR and SEM-EDS. The most important test in macrography testing is the compressive strength test, which is an important index to test whether the concrete material has research significance. Microcosmic tests is an auxiliary means, which can understand the mechanism of the origin of macrography performance through the microcosmic structure, and improve the macrography performance by changing the microcosmic structure appropriately. We made modified to table 4, and the corresponding modification were marked in red in the manuscript.

7. Response to comment: The curing of the samples is the same as it is in [25]. Please, write it also in your paper. Readers are not going to spend time looking in
other papers to find this information. Why did you choose the same curing as in ref [25]? Please, write your explanation in the paper.

Response: We are very sorry for bringing the difficulties to reviewers due to our writing. Reference [25] is an article published by our research group. The sample preparation technique and curing conditions of this manuscript are the same as those of reference [25]. In order to allow reviewers and readers to find information more intuitively, we have supplemented the experimental process and curing conditions in the manuscript to make it more substantial. The corresponding modification are marked in red in the manuscript.

8. Response to comment: What are the standard curing rooms in paper [25]? What conditions are in these rooms? Temperature? Relative humidity? CO₂? Please, state all these.

Response: We are very sorry for bringing the difficulties to reviewers due to our writing. All samples in this study were cured by standard curing(relative humidity 95±1%, room temperature T=20±2°C). The corresponding additions and modifications are marked in red in section 2.2 of the manuscript.

9. Response to comment: Please write: alkaline activators, and not alkali activators.

Response: Thanks for the guidance of the reviewer. The manuscript has been modified according to your instructions and marked in red.

10. Response to comment: What is liquid? Is that only water? Is that alkali + water? Please, make clear that readers know what is exactly L and what is S?
Response: We are very sorry for bringing the difficulties to reviewers due to our writing details. The liquid-solid ratio is mentioned in the manuscript. Liquid refers to the sum of all liquids in the mixed system, including the external addition of water, water in NS solution, and the H$_2$O in NH solid. Solids refer to the sum of all solids in the mixed system, including coal gangue, fly ash, solids in NS solution and the mass of Na$_2$O solids in NH solids. An explanation of the liquid-solid ratio was added to the manuscript and marked in red.

11. Response to comment: Please, explain how did you mix and make pastes, which sample size was cast for XRD, MAS-NMR, FTIR?

Response: In this research, to test the sodium hydroxide molar concentration, slag content, alkali lye amount and liquid-solid ratio, a total of 19 experiments were carried out, P.O. 42.5 pure cement paste specimen as control specimen. The specific mixing ratio was shown in Table 2. The alkali-activated solutions were prepared 24 hours before use and cooled to room temperature to ensure uniform mixing of activator components and improve polymerization. The NH solutions with different NH modulus should be configured respectively. After cooling to room temperature, the NS solution is mixed with the NS solution according to the mass ratio in Table 2 (manuscript). After mixing coal gangue and slag powder evenly, add alkali activator and stir with cement mixer for 5 minutes, poured the fresh paste into steel dies quickly (40mm×40mm×40mm) and vibrated them for 60 seconds on an electric vibration table to remove residual air. The dies were covered with thin polyethylene films and
cured for 1 day at RH=95±1% and T=20±2°C. They were then demoulded, transferred to standard curing rooms and cured for 3d, 7d and 28 day respectively.

The test samples of XRD, MAS-NMR and FT-IR are all powder samples, particle size greater than 200 mesh. The preparation process: The samples were cored, crushed, end hydration with anhydrous ethanol and dried at 105°C under nitrogen environment for 24h. The samples were grinded with agate mortar powder until they felt no granular sensation, and sifted by a 0.08mm square-mesh sieve. The corresponding modifications are marked in red in section 2.2 and 2.3 of the manuscript.

12. Response to comment: Which standard was used to test compressive strength of the pastes?

Response: A YAW-300 pressure testing machine was employed to test 1d, 3d, 7d and 28d compressive strength of the cube specimens of AACGS cementitious materials. The loading speed ranged from 0.5 to 0.8 MPa/s. Three samples of each mixture proportion were tested, with the experimental values averaged to generate the test value for each mixture proportion. If the compressive strength value of one sample exceeded the median value by 15%, the median value was taken as the compressive strength value of the samples.

13. Response to comment: Do you have a photo of the set up for mini-flow test and paste in fresh state? It would be good to add it to the paper to illustrate how did you
perform fluidity test? Why do you call it actually “fluidity test”? This is just a
workability test what you performed in your work.

Response: Fig.1 shows the standard test mold for fluidity, Standard truncated conical
dies (upper diameter U= 60mm; lower diameter U = 36mm; H = 60 mm) were
selected for the paste fluidity test. The truncated conical dies were placed on the
center of a smooth glass plate, filled with fresh paste, scraped by a scraper and lifted
up vertically (the stopwatch was started at the same time). After the paste flew on the
glass plate for 30s, we measured the maximum diameters in two mutually
perpendicular directions with the ruler and took the average as the fluidity of AACGS.
Each group of specimens was measured three times and average of the three fluidity
results was used as the final paste fluidity.

Fig.1 Standard test mold for fluidity (Standard truncated conical dies (upper
diameter U= 60mm; lower diameter U =36 mm; H = 60 mm))

14. Response to comment: What was the setting time of different pastes? Why you
didn’t measure this? Why you didn’t look at heat of hydration of your pastes? It
would tell you a lot about the kinetics of the reactions in your systems.
Response: Thank you for your suggestion. The setting time of different samples was tested in subsequent AACGS mortar, which will be shown in future manuscripts.

When designing the test scheme, we have considered testing the hydration heat of AACGS cementitious materials. However, after reading relevant references, it is shown that the calorimetry peak can only reflect the wetting and dissolution of particles, showing the precipitation of the initial reaction products, and the actual reaction products cannot be obtained. The reaction kinetics is closely related to the setting time. I will supplement the hydration heat test in the subsequent experiments and analyze the hydration process with the combination of setting time and early polymerization products, and explore the early hydration dynamic characteristics of AACGS. Thanks for the opinions of reviewers, I look forward to having the opportunity to have academic exchanges with reviewers.

15. Response to comment: What is bonding mechanism? Why did you call it as such? What is bonding in the paste? It is rather formation of reaction products that you have studied. Make this clear.

Response: We are very sorry for bringing the difficulties to reviewers due to our writing. This paper studies the reaction process of AACGS binary cementitious materials. It would be better if we substituted “bonding mechanism” for “cementation mechanism”. In the analysis of alkali-activated reaction mechanism, the reaction products and degree of polymerization between silica-alumina coal gangue materials and calcium-silica-alumina slag materials are expounded mainly by means of XRD, FT-IR, 29Si MAS-NMR and SEM-EDS. Therefore, it would be better to change
“bonding mechanism” to “cementation mechanism”. The corresponding modifications are marked in red in the introduction and the section 4.

16. **Response to comment:** Please, can you explain how did you prepare you samples for SEM-EDS analysis?

**Response:** The samples were cored, broken, end hydration with anhydrous ethanol and dried at 105°C under nitrogen environment for 24h. Samples with particle size of about 0.5-1cm were selected for SEM-EDS test. A SU8010 field emission scanning electron microscope was employed to observe surface morphology of the broken specimens. An energy spectrometer was introduced to analyze the microelement content of the specimens quantitatively.

17. **Response to comment:** You can clearly see at the surface of your sample carbonates (Fig 10) which are due to carbonation of not well dry sample (you can see formation of calcite from your XRD results). You have to repeat SEM-EDS analysis. Otherwise, these quality of analysis and photos is not acceptable.

**Response:** Thank you for your suggestion, and your suggestion is also very important. According to the opinions of reviewers, we reanalyzed the SEM images, and discarded the products unrelated to the analysis, and focused on the cementing phase generated between coal gangue and slag. The corresponding modifications are marked in red in manuscript section 3.7.
18. **Response to comment**: Please, can you explain how did you prepare you samples for XRD analysis? How fine (what was the mean particle size of paste powder) were the samples? How did you grind and mill the pastes for XRD powder analysis?

**Response**: The preparation process: The samples were cored, broken or crushed, end hydration with anhydrous ethanol and dried at 105°C under nitrogen environment for 24h. The samples were grinded with agate mortar powder until they felt no granular sensation, and sifted by a 0.08mm square-mesh sieve (particle size greater than 200 mesh).

19. **Response to comment**: Please, can you explain how did you prepare you samples for MAS-NMR analysis?

**Response**: The preparation process: The samples were cored, broken or crushed, end hydration with anhydrous ethanol and dried at 105°C under nitrogen environment for 24h. The samples were grinded with agate mortar powder until they felt no granular sensation, and sifted by a 0.08mm square-mesh sieve (particle size greater than 200 mesh).

20. **Response to comment**: Please, can you explain how did you prepare you samples for FTIR analysis?

**Response**: The sample preparation process of FT-IR analysis is the same as that of MAS-NMR. The preparation process: The samples were cored, broken or crushed, end hydration with anhydrous ethanol and dried at 105°C under nitrogen environment for 24h. The samples were grinded with agate mortar powder until they felt no
granular sensation, and sifted by a 0.08mm square-mesh sieve (particle size greater than 200 mesh).

21. **Response to comment**: Fig 3 please add standard deviations on the plots for compressive strength results.

**Response**: Thank you for your suggestion, and your suggestion is also very important. During the test process, the mean value of the compressive strength of three samples in each group was taken as the compressive strength result of the samples. If the compressive strength value of one sample exceeded the median value by 15%, the median value was taken as the compressive strength value of the samples. No data with an error of more than 15% were found in the test in this manuscript, and the average compressive strength of the three samples was taken as the final compressive strength value. The standard deviation of compressive strength results is shown in Fig.2. The corresponding modifications are marked in red in the manuscript.

(a) different slag content
Fig. 2  Compressive strength of AACGS samples

22. Response to comment: Fig 9 why did you choose these samples for MAS-NMR study?

Response: Thank you for your suggestion. As shown in Fig. 2 of the manuscript, the compressive strength value increases with the increase of slag content. However, when the slag content is 20%, 30% and 40%, the increase range of compressive strength is not much different.
Therefore, three groups of samples with large intensity gradient were selected for testing, so as to make analysis more clearly.

23. **Response to comment:** Fig 10 Why did you make spectra as you did in your photos? Why not point analysis? Why not spectral imaging? Based on one spectrum, you cannot say nothing about composition of the reaction products in your samples. You need deeper analysis per sample. In which mode photos were obtained? BSE? SE? Why cracks are there in the samples? You need to perform better SEM-EDX analysis, current quality is extremely low and not satisfactory for scientific explanations.

**Response:** Thank you for your suggestion, and your suggestion is also very important. The EDS selected in the manuscript is a field emission transmission electron microscope produced by American FEI company. The EDS has an energy resolution of 130eV, which can perform micro-area energy spectrum analysis on points, lines and surfaces. The test process is to select microzone for SEM scanning, followed by EDS element analysis of microzone. In existing papers, the point (at least 50 points) or surface is selected for element analysis. In order to make the test more convenient and accurate, we choose the surface for microzone energy spectrum test.

Melo et al.\cite{1}, Cartwright et al.\cite{2} and Mastali et al.\cite{3} showed that the shrinkage value of alkali-activated materials was larger than that of pure cement materials, and several micro-cracks could be clearly seen in SEM photos may be caused by shrinkage during curing.
We realized that our analysis in section 3.7 was not enough, and quality is extremely low, so we reanalyzed SEM images in depth, added element table of EDS, and analyzed the changes of elements in the manuscript. The specific modifications are marked in red in the manuscript.


24. Response to comment: Hydration of AACGS polymers? Please make distinction between cement that can hydrate and alkali activated materials which are not only hydrating but polymerizing and condensing.

Response: The chemical reaction process of alkali-activated cementitious materials is different from that of cement. The chemical reaction process of alkali-activated cementitious materials involves condensation polycondensation and reorganization of Si-O and Al-O bonds, and what happens is the polymerization reaction. A large number of references still show that the alkali activation process is hydration, and a small number of papers are called geological polymerization reaction or polymerization reaction. For example, references[4,5].

25. **Response to comment:** What is an appropriate amount of slag instead of coal gangue that provides additional CaO?

**Response:** Slag is a cementing material of calcium, silicon and aluminum, which contains a lot of active CaO(38.43%). Coal gangue is a kind of silica-aluminum cementing material with very low CaO content(0.62%). Appropriate amount of slag replaces coal gangue, so that CaO in the slag can accelerate the alkali activated polymerization process and improve the compressive strength of AACGS cementitious materials. In order to make the conclusion more clearly, we proofread and modify the conclusion, highlighting the significance of the research and important research results. The relevant modifications are marked in red in the manuscript.

26. **Response to comment:** Main hydration products of AACGS polymers include N-A-S-H gels, C-A-S-H gels and some other alkaline aluminosilicate gels. What are other alkaline aluminosilicate gels?

**Response:** The XRD phase analysis of AACGS shows that the main characteristic peaks include CaAl5Si2O10·4H2O, NaAlSiO2·H2O and AlSi2O5·xH2O. In addition to sodium aluminosilicate and calcium aluminosilicate, there are aluminosilicate gels. AACGS in the polymerization process to generate amorphous aluminum silicate polymer, gelatinization generated amorphous aluminum silicate colloid, converted into "zeolite" phase, sodium aluminum silicate and calcium aluminum silicate and aluminum silicate colloid both belong to the "zeolite" phase.
order to make the statement more professional, we revised the statement in the
manuscript, and the corresponding modification are marked in red.

**27. Response to comment:** How did you identify N-A-S-H gels? Where are detailed
EDX analysis?

**Response:** Sodium aluminosilicate hydrate (N-A-S-H) gel, the main reaction product
of the alkali-activated alumino-silicates. With the increase of slag dosage, the
concentration of Ca²⁺ in the alkali-activated cementing system increases, and the
amount of catalytic formation of C-(A)-S-H increases. XRD analysis shows that the
main characteristic peaks include SiO₂, Ca₅Al₂Si₂₀O₄₀•₄H₂O, NaAlSiO₂•H₂O and
Al₂SiO₅•xH₂O, that is to say, the reaction products of alkali-activated contains N-A-S-
H gels and C-A-S-H gels. According to the opinions of reviewers, we analyzed EDS
in detail, as shown in table 5 of the manuscript, and the corresponding modifications
are marked red in the manuscript.

<table>
<thead>
<tr>
<th>At%</th>
<th>Si</th>
<th>Al</th>
<th>Ca</th>
<th>Na</th>
<th>O</th>
<th>Ca/Si</th>
<th>Si/Al</th>
<th>(Ca+Na)/(Si+Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0-12M2- 36</td>
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<td>2.09</td>
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<tr>
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<td>10.08</td>
<td>1.82</td>
<td>50.28</td>
<td>0.424</td>
<td>1.694</td>
<td>0.315</td>
</tr>
</tbody>
</table>

**28. Response to comment:** How did you study the charge density of the cation?

**Response:** We are very sorry for bringing the difficulties to reviewers due to our writing.
We did not test the charge density of the cation. The experimental analysis shows that when the content of slag is 0%, only Na cation is contained in the alkali-activated gangue and slag cementation material system. With the increase of the content of slag, a large number of CaO participate in the alkali-activated reaction and gradually introduce Ca cation, which changes the cationic environment in the system and increases the concentration of Ca$^{2+}$. Garcia-Lodeiro et al.\cite{Garcia-Lodeiro2011} found that Ca$^{2+}$ ions in slag promoted the exchange of Na$^+$ ions, and the product changed from N-A-S-H gel to C-A-S-H gel. In order to make it more clearly, we modified the conclusion and marked it in red in the manuscript.


Thank you very much for your letter and advice on our manuscript. We quite appreciate your favorite consideration and the reviewer’s insightful comments. We tried our best to improve the manuscript and made a little changes in the manuscript. These changes will not influence the content and framework of the manuscript. We did list the changes and marked in red in revised manuscript(except grammatical and English language). We appreciate for Editor Icy Liu and Reviewers warm work earnestly, and hope that the correction will meet with approval.

Once again, thank you very much for your comments and suggestions. We hope that the revision is acceptable and look forward to hearing from you soon.
With best wishes,

Ma Hongqiang, Zhu Hongguang*, Yi Cheng, Fan Jingchong, Chen Hongyu, Xu Xiaonan and Wang Tao

Jun 26, 2019