RINOPOLYCRETE - TOWARDS A CEMENT-FREE AND FULLY RECYCLED CONCRETE

PROJECTO FCT

PTDC/ECI-COM/29196/2017

Recycled inorganic polymer concrete - Towards a cement-free and fully recycled concrete
(RInoPolyCrete)

Task 4 - Report I

Lessons learned from the preliminary stage of the experimental campaign

August, 2019

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Acronyms

AAM	Alkali-activated materials
EAFS	Electric arc furnace slag
EDS	Energy dispersive X-Ray spectroscopy
FA	Fly ash
ITZ	Interfacial transition zone
LCA	Life cycle assessment
MIBA	Municipal solid waste incinerator bottom ash
NaOH	Sodium hydroxide
pH	Hydrogen potential
RA	Recycled aggregates
SEM	Scanning electron microscopy
WTS	Water treatment sludge
WTSA	Water treatment sludge ash
XRD	X-ray diffraction
XRF	X-ray fluorescence

1 Introduction

This report contains a summary of the knowledge gathered throughout the preliminary experimental trials, MSc theses and literature reviews on the use of municipal solid waste incinerator bottom ashes (MIBA) as precursor for the production of alkali activated materials (AAM). The present report is divided in several sections regarding specific aspects worthy of observation throughout the experimental investigation. They concern the aluminosilicate precursors used as binder for AAM, the alkaline activators, the role of the water reducing admixtures, the mixing methodology that needs to be adopted depending on the material used, thermal curing conditions, pH of AAM and the influence of adding recycled aggregates (RA). The main objective of this report is to provide the authors' insight gained along this process in a simple manner and to establish specific research objectives for future campaigns.

2 Precursors for alkali activation

2.1 Waste precursors for alkali activation

The following waste by-products were evaluated as potential precursors for the production of AAM within the RINOPOLYCRETE project:

- **Electric arc furnace slag (EAFS)**: it is one of the by-products of the steel smelting in the Siderurgia Nacional de Portugal, provided by HARSCO.

- **Municipal solid waste incinerator bottom ash (MIBA)**: it was gathered from the incineration of solid waste from the Valorsul treatment plant, located in São João da Talha, in the municipality of Loures, Portugal.

- **Water treatment sludge (WTS)**: pre-dried sludge from the potable water treatment plant in Lisbon (Empresa Portuguesa das Águas Livres - EPAL SA) that was collected from the output of the sedimentation stage.

- **Water treatment sludge ash (WTSA)**: sludge from EPAL, described in the previous bullet point, and incinerated at about 700 °C.

Fly ashes (FA), which are not considered a waste but rather an extensively marketed by-product, have been extensively researched and will be used to produce control AAM mixes.

2.2   Treatment process

The aforementioned materials usually come in an unprocessed form and need treatment prior to their use as precursor. Not only do they contain a noteworthy amount of moisture, which needs to be removed by placing them in an oven at ≈105 °C, but they may also present considerable particle size. To be used as precursor and thus as complete cement replacement, the particle size needs to be substantially reduced by means of ball milling, which is the most effective method and also typically used for clinker size reduction. The time of a given precursor inside such machine should ensure an average particle size of 50 μm. This comminution is likely to be easier for MIBA when compared to EAFS, which is denser and harder to break down. The optimum time for each precursor in the ball mill machine for a specific grading size is unknown; a specific study would be required involving different milling times and laser particle size distribution analysis. However, one hour of ball milling was found to be enough for a considerable reduction assuming previous fragmentation by means of Los Angeles (LA) abrasion test has been applied.

Unlike the other wastes, MIBA contains a notable amount of non-friable material (i.e. paper, plastic, metal, wood, etc.), which needs to be removed prior to ball milling. This can be made by initially subjecting MIBA to a quick grinding process (e.g. LA abrasion machine for 15-20 minutes) capable of transforming it into a fine sand. Afterwards, the non-friable material can be removed by passing the ground material through a 1 mm sieve. The material above that size can be considered waste, whereas the rest can then be subjected to ball milling.

One possible method to further improve the quality of MIBA would be to wash it prior to the aforementioned grinding processes. It would reduce organic matter, soluble chloride and sulphate ions and other unnecessary particles capable of hindering the alkali activation process. This is an untested idea within the RINOPOLYCRETE project, but that has shown promise in other studies.

WTS, in spite of the existence of some amorphous phases, cannot be used as activator, as demonstrated in a preliminary test; it behaved as a sand instead of a binder when attempting

alkali activation. WTS **will no longer be considered for future evaluation**. WTSA, on the other hand, presents a considerably larger fraction of amorphous material capable of being activated and could show potential as precursor. Nevertheless, since it needs to be subjected to a 700 °C thermal treatment process (at least), additionally to the treatments it already receives, its use as precursor for AAM would likely lead to poor results from a life cycle assessment (LCA) perspective and thus **will no longer be considered for future evaluation**.

2.3   Characterization tests

The use of aluminosilicate waste as precursors for the production of AAM means that integral replacement of cement will be made and, consequently, a full battery of basic characterization tests are required. These include electron microscopy coupled with energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), X-ray fluorescence (XRF), laser particle size distribution and BET surface area. Owing to the specific characteristics of the mentioned waste precursors, pH level, metallic Al quantification and pozzolanic activity with the modified Chappelle test should also be carried out.

The results obtained thus far on MIBA suggest that it may contain a high SiO_2 content and a reasonable amount of Al_2O_3. However, these compounds exist in slightly different forms, some of which crystalline, whereas amorphous phases would be ideal for AAM production. Still, using the modified Chappelle test, it was observed that, even though MIBA may present lower pozzolanicity when compared to FA, it contains some amorphous compounds. Further analysis to these phases should include an exact quantification using the e.g. Rietveld method using the XRD analysis. However, this has proved difficult within IST, as none of the equipment is prepared for this method. This issue needs to be resolved by outsourcing.

The metallic Al quantification proved to be an interesting and accurate method to measure the amount of Al in MIBA and exactly how much H_2 gas can be produced in a given mix; for example, in 1 kg of a specific type of MIBA, 6.3 l of H_2 gas was produced, which has severe consequences on the properties of the final material. This method should be further developed and used to characterize all MIBA samples. Furthermore, there is considerable potential to

develop a specification for this test as it does not exist to the best of the authors' knowledge.

The modified Chappelle test has shown good results in quantifying the reactive fraction existing in MIBA. However, some concerns exist on the reaction between the Ca-bearing phases and the HCl acid, which might lead to a greater than expected consumption of material, thus leading to an inaccurately higher value indicating higher pozzolanicity.

3   Alkaline activator

3.1   Type

Although there are other types of activators, the ones used in the RINOPOLYCRETE project were sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3). Not only are these more cost-effective, but they are easier to acquire and are typically used in the academia in the study of AAM thereby allowing adequate benchmarking.

High quantities of NaOH can be directly purchased at a reasonable price, but Na_2SiO_3 may be costlier. Also, it contains an uncontrolled amount of SiO_2, which hinders stoichiometry calculation and prevents adequate analysis of the results when looking at the materials' chemical composition. The synthesis of Na_2SiO_3 with the use of silica gel and NaOH was found to be a more cost-effective and controllable alternative.

3.2   Concentration

In the two MSc thesis completed within the scope of the RINOPOLYCRETE project, alkaline solutions with a NaOH concentration of 10 M were used for most mixes (8 M and 12 M concentrations were also used). It is the most typically used concentration in the literature and should be used in the RINOPOLYCRETE project for comparison purposes.

In the preliminary trials of the RINOPOLYCRETE project, NaOH was used to prepare 2.5 M solutions. This is a low concentration in comparison with that typically practiced in the literature (i.e. 10 M). It was selected due to the high calcium content in MIBA and EAFS, which is insoluble in high concentrations of NaOH. Nevertheless, it is likely that this concentration is too small to result in a strong alkaline environment capable of adequately dissolving amorphous

silica and alumina phases; in two separate occasions in the RINOPOLYCRETE project, enhanced mechanical performance was observed in mixes with higher concentration of NaOH. Therefore, future trials will be carried out to ascertain the optimum concentration levels.

When synthesized Na_2SiO_3 was used to produce AAM, unexpected results were obtained. Theoretically, the higher content of SiO_2 in this activator would contribute to the overall SiO_2 content of the inorganic polymer chains and thus to the strength of the final material. However, not only was the mechanical performance worse than that of mixes using only NaOH, but there was a considerable loss of mass during the demoulding process. It is likely that this type of activator may have reacted with the release agent, removing its primary function and thus resulting in specimens adhered to the mould. Naturally, owing to the loss of material, these specimens showed lower flexural and compressive strengths. Future trials will still make use of the synthesized Na_2SiO_3 as it is known to produce AAM with enhanced mechanical performance. However, smaller quantities of silica gel will be used to determine whether the mortar specimens can be properly demoulded without mass loss. Furthermore, a commercially available Na_2SiO_3 will be acquired and compared with an equivalent synthesized Na_2SiO_3 to understand potential implications to performance.

4 Water reducing admixtures

The following water reducing admixtures (WRA) were used in the preparation of mortars within the project: polycarboxylate, lignosulfonate, naphthalene and melamine. Control mortars without WRA were also tested. Although the use of WRA is pointless in the production of AAM using conventional FA, as this material offers high workability due to its spherical particles' shape, MIBA-based AAM required WRA. Not only are MIBA particles irregular and angular (Figure 1), thus increasing inter-particle friction, but initial trials in the project suggested that this ash is somewhat hydrophobic; mixing the ashes with water leads to the formation of agglomerates, thereby hindering the mixes' workability and preventing the alkali activation reaction from taking place. For this reason, the use of a WRA as a surfactant (wetting agent) was found to be an absolute necessity to promote the reaction between the amorphous phases in MIBA and the OH^- ions in the alkaline solution.
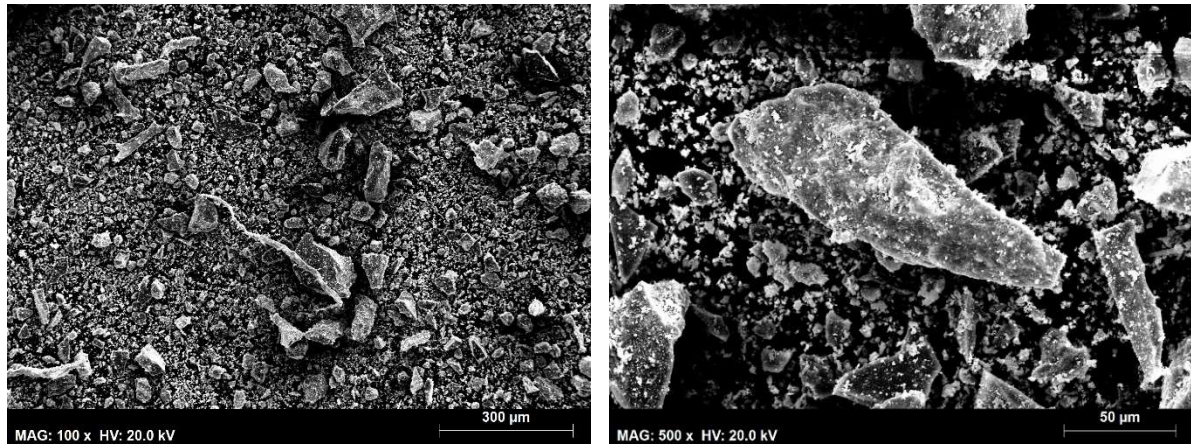
Figure 1 - SEM micrographs of MIBA

Not all of the aforementioned WRA can be used in AAM. Due to the extreme pH conditions, the chemical structure of some WRA degrades thereby removing its effectiveness as wetting agent/workability inducer. For example, polycarboxylate (Figure 2) and melamine were found to provide little additional workability, whereas lignosulfonate and, especially, naphthalene are more stable in high pH environments and capable of resulting in homogenous mixes. Although future campaigns will focus on the use of naphthalene as WRA, as it was found to provide the best results, a parallel campaign on the influence of the use of different WRA on the rheology of alkali activated MIBA would be an interesting research idea to follow through.

Figure 2 - Mortar using a polycarboxylate-based WRA

Although the use of WRA is mostly looked at to provide workability and thus used at the end of the mixing process, in the case of mixes with MIBA, its incorporation should be made at the very start of the process to provide a "wetting effect" of the metallic Al particles. These should come into contact with the alkaline solution as soon as possible to initiate corrosion and release H_2 gas. Otherwise, non-wet Al particles might react further ahead in the curing process.

5 Mixing methodology

Although AAM can be produced in the same way as conventional mortar and concrete, due to the composition of MIBA, some changes must be made in the production process of mixes containing it. MIBA contains notable quantities of metallic Al, which corrodes in a high pH environment (created with the use of a NaOH solution). This leads to a considerable production of H_2 gas, which becomes trapped in the fresh mix, resulting in excessive porosity (Figure 3) and thus loss in mechanical performance.
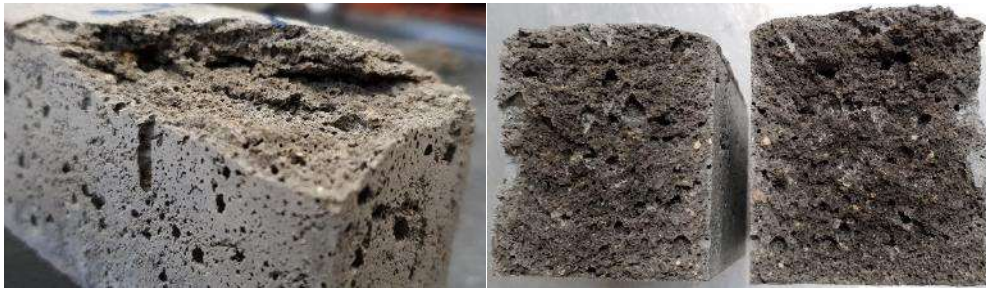

Figure 3 - Specimens with high porosity due to entrapped H_2 gas in fresh mixes

The initial idea to solve this issue was to reduce the presence of metallic Al by means of an Eddy current electromagnetic separation stage for non-ferrous metals. However, research has shown that the efficacy of this separation process is seriously compromised by the size reduction of the metallic Al particles making integral extraction impossible. Still, completely removing the Al fraction would result in a precursor with little amount of Al-bearing phases available to react, thus resulting in less inorganic polymer compounds. Therefore, the idea of completely corroding metallic Al came up. The reaction between metallic Al and NaOH leads to the formation of compounds that can be used in inorganic polymer reactions. In other words, instead of looking at Al as a contaminant in MIBA, its full corrosion can be potentiated, the products of which can actively participate in the AAM's strength development.

To solve the H_2 gas production problem, several methodologies were tried to determine the optimum mixing method of MIBA with the alkaline activator and the fine aggregates. Initially, conventional mixing methods were tested, where 2/3 of the alkali activator was mixed with the precursor and the rest containing a WRA. However, it was later observed that further mixing time

would be required for a greater part of H_2 gas to be released and the WRA should be added at the begging to wet all particles. Other iterations involved the application of a resting time of 15-45 minutes to promote H_2 gas release. However, the expansion of specimens was still observed.

The incorporation of Na_2SiO_3 led to a change in the mixing method as well. An extremely fast setting of the mix was observed three minutes after the start of the mixing process. It is possible that there is an uncontrolled formation of initial C-S-H gel through the reaction of free Ca^{2+} ions of the precursor and the SiO_3^{2-} ions of the alkaline activator, thus leading to an unworkable mix. To prevent this, the precursor should be mixed with the alkaline solution alone for some time (5-15 minutes) prior to the addition of any aggregates. The formation of the mentioned compounds will still be observed, but continuous mixing will result in their breakdown, which could not be verified with the additional shear resistance prompted by the existence of aggregates.

Other mixing methodologies included the following:

- The alkaline solution was prepared 24 hours before the preparation of mortars. The aggregates were added 30 s after mixing MIBA with the alkaline solution, then 15 min of mixing combining slow and fast agitation, finally 45 min resting;
- The alkaline activator was prepared 24 hours before the preparation of mortars. 15 min of mixing MIBA with the alkali solution in rapid agitation, then 45 min resting. Finally, the aggregates were added and mixed for 5 mins;
- The aggregates were added 30 s after MIBA with a cold alkaline activator (4 °C) using slow mechanical stirring, then 15 min of fast mixing;
- The alkaline activator together with MIBA were heated at 80 °C on a magnetic plate for 2 hours, then left for 2 more hours and finally mixed with the aggregates for 5 min;
- The alkaline activator was prepared and MIBA was immediately added, then the mix was left to rest for 24 hours. After that, it was mixed with the aggregates for 5 min;
- The alkaline activator was prepared with hot water at 50 °C. A temperature of 80 °C was reached when adding solid NaOH and immediately mixed with MIBA for one hour plus one hour of rest. Finally, the aggregates were added and mixed for 5 min.

The method capable of delivering specimens with better mechanical performance was the second to last, wherein the MIBA and alkaline solution were left to react for 24 hours. This method has some advantages. First and foremost, it apparently ensured that the H_2 gas release would be complete, thereby preventing additional porosity from it. Additionally, the alkaline activator does not have to be heated prior to the mixing process (i.e. no added energy) in order to potentiate the gas' release; the metallic Al's exposure to the high pH environment for 24 hours is sufficient. From an industrial perspective, this method, despite slow, can be easily applied in a larger scale, wherein the mix without aggregates can be produced 24 hours in advance to its casting and stored in large sealed vats capable of harnessing the released H_2 gas. However, the water loss over the course of 24 hours was not registered and needs to be compensated to ensure target liquid to solid ratio; future campaigns will take this factor into consideration.

The use of EAFS for AAM production, which, in the beginning, was merely an exploratory idea, showed a considerable improvement in mechanical performance when compared with the best iteration of MIBA-based AAM. It is currently being used in the industry as an aggregate, but, in the light of these findings, it can be used as the integral binder in AAM production with minimum changes to the mixing methodology of conventional mortar and concrete. Additionally, contrary to expectations due to EAFS's irregular shaped particles (Figure 4), it delivered mixes with significantly better workability, thereby allowing the reduction of water in the system. Therefore, future research should be carried out on this material.
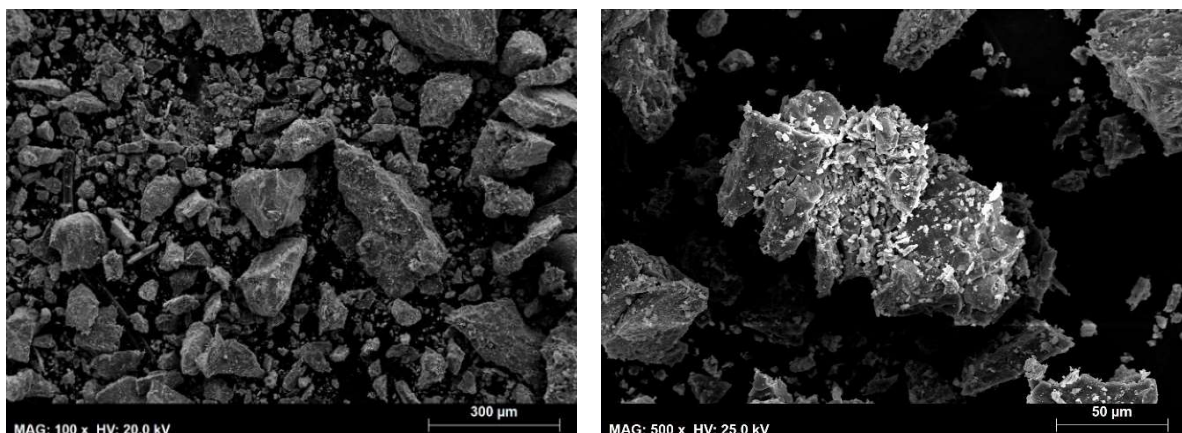

Figure 4 - SEM micrographs of EAFS

6 Curing conditions

Throughout the preliminary trials, it was established that applying a thermal curing regime to MIBA-based AAM is essential. Attempts were made to obtain a hardened specimen cured in a laboratory environment; however, after 7 days of curing, these specimens showed minimum setting. From an industrial point of view, even if they would show adequate hardening after a reasonable period of time, the slow rotation of moulds would render it impractical and unsustainable. Therefore, **any future attempts to produce MIBA-based specimens in ambient conditions are strongly discouraged**.

Four different thermal curing regimens were tested throughout this project: 70 °C for 24 hours; 80 °C for 24 hours; 90 °C for 24 hours; and 70 °C for 48 hours. All conditions led to the production of specimens with some mechanical performance. However, the first one, having the lowest amount of energy introduced in the system, resulted in slightly decreased mechanical performance in comparison with the other regimens. Still, it was also observed that, after a reasonably long period of time, there was greater strength development. This infers that the thermal activation with lower amount of energy results in the incomplete dissolution and precipitation of inorganic polymer chains, the rest of which occurs over time.

As expected, higher temperatures and exposure time led to enhanced mechanical performance. However, even though there was greater incorporated energy from the 70 °C for 48 hours when compared to the 90 °C for 24 hours regime, the latter delivered AAM with better results. Therefore, it is best to cure specimens at a slightly higher temperature but for a smaller period of time, which is expectably better from an LCA perspective.

Although the 90 °C for 24 hours regime resulted in specimens with reasonable performance, it also involves the use of a greater amount of energy and there are constraints in the newly built thermal curing chamber in the laboratory. Until certainty is gained concerning the chamber's stability when at 90 °C, all mixes will be produced at a temperature of 80 °C. Not only is this temperature capable of producing AAM, but it is also the most widely used temperature in the literature, thus allowing benchmarking.

7 pH of AAM

The pH of AAM is obviously high at the beginning. However, carbonation tests have shown a considerably fast decrease in pH after a short period of time, which shows serious limitations of AAM, regardless of the binder in the production of structural concrete. Therefore, it would be interesting to study the development of this property over time with ensuing polymerization.

8 Recycled aggregates

Only one experimental campaign was carried out thus far involving the use of recycled aggregates (RA) from crushed concrete in the production of MIBA- and FA-based AAM. When compared to control mixes without RA, the mechanical performance strongly decreased. Though some decrease was expected, in some cases, there was a ~80% loss in compressive strength. Assuming that the RA-containing AAM were correctly made, it is possible that the loss in performance is due to the lack of reaction by RA with the alkaline activator resulting in the lack of an adequate interfacial transition zone (ITZ), whereas in the case of siliceous aggregates there is probably some reaction thus improving the adhesion between the binder and aggregate. Nevertheless, there is reason to believe that further improvement can be achieved and thus future campaigns should focus on the use of RA for the production of AAM.

9 Variables to use in upcoming campaigns

9.1 Precursors

MIBA is be the main waste precursor under study in this project. Four types of MIBA, gathered from piles and produced in different months of the year (September 2018, October 2018, December 2018, and January 2019) will be evaluated.

EAFS was also identified as a potential precursor for AAM production. Although less attention will be granted for this material since it is not the theme of the project, it does, however, fit in some parts of the project's plan submitted to FCT as partial and complete MIBA replacement as precursor. Since it has shown high reactivity, parallel campaigns should be carried out to understand the potential of EAFS.

The precursors must be submitted to an initial size reduction by means of LA abrasion and, subsequently, a ball milling process to reduce their size to a point that it is comparable to that of cement. 15 min to 20 min of LA abrasion + 60 min of ball milling is expected to be enough.

9.2 Variability of MIBA

A specific campaign will be devised, wherein the full characterization of MIBA will be made (section 2.3), as well as its influence on the basic properties of alkali activated mortars. One of the MIBA samples was gathered in a greater amount and will be used for further evaluation in other variables and in the production of concrete.

9.3 Mixing methodology

The mixing approach for conventional mortars was adapted taking the presence of metallic Al into account. MIBA and the WRA-containing alkaline activator are mixed for 15 minutes and then left to rest for 24 hours to promote the release of H_2 gas. After that, the lost water content must be measured, compensated and then the aggregates should be introduced in the mix.

9.4 Water reducing admixture

All MIBA-based AAM must contain a WRA. It should be a naphthalene-based commercially available WRA for concrete. An initial WRA content of 1% by binder content will be fixed initially, but may be subjected to change depending on the workability it offers.

A parallel campaign is also expected to be carried out on the effect of different types of WRA on the rheology of alkali activated mortars.

9.5 Concentration of the alkaline activators

NaOH and Na_2SiO_3 will be used as activators to produce AAM. An initial stage will determine the optimum concentration of NaOH for January 2019 MIBA. The molarities will be of 4 M, 6 M, 8 M and 10 M for the NaOH activator. For a specific ratio of Na_2O to binder content established in the previous part, the SiO_2/Na_2O ratio will vary between 0.25, 0.50, 1.00 and

1.50, to understand the implication of adding additional SiO_2 into the system in terms of mechanical performance.

Concerning the liquid to solid ratio, although it would be preferable to maintain a constant value, there are other factors involved, including the Na_2O/binder content ratio, which need to be fixed after establishing its optimum content. Still, a constant amount of water must also be fixed throughout the mixes. However, this would mean that the volume of alkaline solution would vary. Further analysis to this regard is required.

9.6 Curing regimens

A specific campaign will be carried out on the influence of the thermal curing regimens on the performance of alkali activated mortars using the optimum concentration of alkaline activators established in the previous campaign. The following regimens will be assessed: 50 °C for 24 hours; 50 °C for 48 hours; 50 °C for 72 hours; 80 °C for 24 hours; 80 °C for 48 hours; 80 °C for 72 hours. Temperatures above 80 °C might prove to be an impossibility in the thermal curing chamber due to the instability of extruded polystyrene (XPS) boards.

9.7 Recycled aggregates

RA from a construction and demolition waste recycling plant will be used as complete natural aggregate replacement. Some of these aggregates might show more positive results in comparison with recycled concrete aggregates since they contain a notable amount of masonry-based fragments, which typically present some pozzolanicity. Replacement levels of 50% and 100%, by volume, will be used. Nevertheless, these RA will only be applied further ahead in the investigation, after the aforementioned variables have been tested.

9.8 Additional research ideas for MIBA-based AAM

AAM are known for their great resistance to high temperatures. It would be interesting to understand the properties of MIBA-based AAM after being subjected to fire and compare its properties with conventional concrete exposed to the same conditions.

AAM also present high resistance to chemical attack. Expansion due to exposure to magnesium and sodium sulphate would be an innovative approach and might show positive results in terms of valuable applicability of the material in environmental conditions in which conventional concrete usually presents low resistance.

Washing MIBA is likely to significantly reduce organic matter content that hinder the polymerization process. Despite the obvious environmental impacts involved, a parallel campaign studying the influence of washed vs. unwashed MIBA could be interesting to understand this applicability of this treatment process to improve the performance of AAM.

To the best of the authors' knowledge, there are no standards or specifications with test methods assessing the amount metallic aluminium in MIBA. Further ahead in the project, it would be of interest to further develop the method in order to understand reproducibility, representative testing variables and limitations of the method.

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