A Wood-to-Wood Cascade Upcycling Valorisation Approach

WOOD2WOOD

» Deliverable 11.2

Valorisation of ashes from CDW and thermal gasification (version 1)

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GLOSSARY OF ACRONYMS

Acronym	Extended Definition
W2W	Wood2Wood
CDW	Construction & Demolition waste
FA	Fly ash
C-S-H	Calcium Silicate Hydrate
SEM	Scanning Electron Microscopy
EDX	Energy-Dispersive X-ray spectroscopy
ICP	Inductively Coupled Plasma Spectroscopy
PCBs	Polychlorinated Biphenyls
HTC	Hydrothermal Carbonization
HT	Hydrothermal treatment
XRD	X-ray Diffraction
FTIR	Fourier-Transform Infrared Spectroscopy
GC-MS	Gas Chromatography – Mass Spectrometry
MSWI-FA	Municipal Solid Waste Incineration Fly Ash
DoE	Design of Experiments

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Executive summary

This deliverable reports the progress made under Task 11.3 – *Valorisation of Ashes from CDW and Thermal Gasification* during the first project period (M08–M18) of the W2W project. The objective of this task is to transform biomass-derived fly ashes, which contain toxic heavy metals and persistent organic pollutants, into stabilized aluminosilicate structures using microwave-assisted hydrothermal treatment.

During this period, the focus of the task was on establishing the baseline for the design and execution of a parametric experimental matrix, aimed at determining the optimal conditions (temperature, NaOH concentration) for the formation of zeolitic and calcium silicate hydrate (C–S–H) phases from biomass incineration fly ashes. Key activities included:

- Comprehensive literature review of relevant hydrothermal valorisation processes.
- Design of Experiments (DoE) covering temperature and NaOH influence.
- Development of the experimental campaign
- Morphological and elemental characterization of the treated ashes using SEM and EDX, identifying the formation of key mineral phases.

The results achieved demonstrate a clear temperature- and alkalinity-driven mineral evolution. The key findings from this initial phase are summarized below:

- At lower temperatures (175 °C) and alkalinity (0% wt. NaOH), C–S–H gels and tobermorite apparently dominate.
- At higher temperatures (≥200 °C) and NaOH content (30-60% wt. NaOH), zeolitic structures that could correspond to analcime and cancrinite, are increasingly formed.
- According to the literature, these structures are of interest for immobilising heavy metals and adsorbing PCBs.

Based on the first promising results obtained, the work for the next period (M18–M36) will approach the following actions:

- Further characterisation of the zeolitic structures through quantitative phase identification, including X-ray diffraction (XRD) and FTIR to validate SEM–EDX interpretations.
- Leachability tests to assess the immobilisation efficiency of heavy metals (Pb, Zn, Cd, Cu) in the new mineral structures.
- Analysis of dioxins and PCBs, using GC–MS and internal standards.

This first stage demonstrates that microwave hydrothermal treatment is a technically viable valorisation pathway for biomass fly ash. By adjusting reaction parameters, the process can be steered toward mineral structures with distinct stabilization functions, supporting the development of a circular, low-impact management strategy for hazardous combustion residues.

This deliverable presents a public summary of the activities and findings developed under the framework of W2W project. While the document itself is classified as public (PU) in accordance with the Grant Agreement, it is important to note that the outcomes discussed are the result of extensive

experimental work that has generated a significant volume of confidential data and internal analyses. Due to the sensitive nature of the technical details and potential implications for intellectual property or strategic developments within the consortium, the complete dataset and in-depth results remain confidential and are accessible only within the consortium, particularly at CIRCE and relevant partner institutions. These detailed materials can be shared upon justified request, subject to appropriate confidentiality agreements, to ensure responsible and secure dissemination of knowledge while protecting the interests of the project partners

1. INTRODUCTION

Biomass combustion serves as an important source of renewable energy in the European energy mix, contributing to the decrease of the dependence on fossil fuels while diminishing the emissions of greenhouse gases. Recent reports indicate that biomass represented about 60% of renewable energy in the European Union in 2022, with waste wood significantly contributing. Waste wood is an abundant and carbon neutral source for such issue [1]. However, biomass combustion generates considerable quantities of residues ash, such as bottom ash and fly ash, which pose environmental and disposal difficulties. Specifically, fly ashes which generally consist of fine particles gathered from exhaust gas filtration systems, can have high concentrations of toxic heavy metals like lead (Pb), zinc (Zn), cadmium (Cd), copper (Cu), and chromium (Cr), or other persistent organic pollutants such as dioxins [2].

The valorization of ashes from biomass incineration corresponds with the principles of the circular economy and sustainable resource management, intending to transform these byproducts from waste flows into useful products or materials [3]. Traditional handling of fly ash typically involves regulated landfilling because of concerns regarding their toxicity and potential leachability, leading to significant environmental and financial burdens [4]. Consequently, creating sophisticated technologies that can stabilize or immobilize dangerous substances while retrieving functional materials is critically important.

Hydrothermal treatment methods have surfaced as effective approaches for ash valorization, providing gentle reaction conditions to convert ash minerals and encapsulate heavy metals by crystallizing stable phases. Particularly, the hydrothermal synthesis of tobermorite and zeolite-like phases is of interest due to their dual functionality in immobilizing heavy metals and adsorbing organic contaminants [5]. Tobermorite, a mineral of calcium silicate hydrate, demonstrates outstanding cation exchange and encapsulation characteristics, while zeolites offer highly porous structures that are efficient for capturing heavy metals and diminishing organic toxins like dioxins [6–8]. However, traditional hydrothermal treatments are often time-consuming and energy-intensive, limiting their scalability.

Microwave-assisted hydrothermal valorisation introduces significant process intensification by enabling rapid and volumetric heating, which can enhance reaction kinetics, reduce treatment times, increase efficiency for an intensive energy process and improve crystallinity of target phases, therefore presenting strategic advantages. [6,9] This approach has been successfully applied in various mineral synthesis and waste valorisation contexts but remains underexplored for biomass incineration fly ashes [10]. A comprehensive literature survey reveals a notable research gap in studies combining microwave hydrothermal methods with ash valorisation targeting tobermorite or zeolite-like phases specifically for heavy metal immobilization and dioxin content reduction. Most existing works focus either on coal fly ashes or municipal solid waste, and most without microwave enhancement [11,12].

Addressing this gap, the present study explores the synthesis of tobermorite and other zeolite-like structures via microwave hydrothermal treatment of biomass incineration fly ashes, emphasizing waste wood as a key feedstock typical of European biomass energy facilities. We aim to evaluate

the potential of this novel valorisation route for effective immobilization of heavy metals such as Pb, Zn, Cd, Cu, and Cr, and to investigate preliminary effects on dioxin reduction. The initial phase, reported herein, comprises a detailed literature review, design of experiments to optimize process variables, experimental synthesis trials, and characterization of the products by scanning electron microscopy (SEM). This work lays the foundation for the next stage, where the produced structures will be assessed in terms of inorganic immobilisation and dioxin reducing potential, advancing microwave hydrothermal valorisation as a sustainable strategy for ash management, contributing to circular economy goals by transforming hazardous residues into functional, stabilized mineral phases suitable for reuse or safe disposal.

2. OBJECTIVES

The objective of the task T11.3, reported in this deliverable, is to valorise ashes from biomass combustion, a typical residue of the wood valorisation process. The fly ashes from biomass combustion have been gathered and made to react in basic conditions under microwave heating to generate zeolitic-type structures capable of immobilizing different types of contaminants.

The main objective of the task and of the work carried out in this first stage has been to find the experimental conditions that allow the production of these zeolites under microwave-assisted hydrothermal treatment. To this end, a literature review was conducted to identify the most suitable experimental conditions, which were subsequently screened through controlled experiments.

The generated results have been studied by SEM microscopy to confirm the production of these zeolitic structures. Further quantification of these structures will be conducted in the next project period.

3. METHODOLOGY

3.1. DESIGN OF EXPERIMENTS & LITERATURE REVIEW

Firstly, in order to establish the operating conditions for generating zeolite-type structures from an ash stream, a literature review was carried out. The aim was to find the operating conditions for the hydrothermal treatment of this waste, particularly a range of parameters, including different temperatures, residence times, concentrations of basic compounds, or amounts of external compounds (such as silica) to optimise the production of these structures.

For example, Wang et al. (2022) investigated the hydrothermal synthesis of tobermorite from coal fly ash as a valorisation route for this industrial waste. The process involved mixing fly ash with calcium oxide and a sodium hydroxide solution (20 g/L Na_2O) at a liquid-to-solid ratio of 20 mL/g and a $CaO:SiO_2$ molar ratio of 1.0, followed by hydrothermal treatment in an autoclave at temperatures ranging from 180 °C to 260 °C for 4 hours. The study identified 180 °C as the optimal temperature to maximize tobermorite formation, yielding porous pellet-like particles composed of nanosheets and nanofibers. This morphology resulted in a significant increase in specific surface area (29.98 m^2/g) and pore volume (0.1325 cm^3/g) compared to raw fly ash, confirming the development of a mesoporous structure. Higher temperatures led to the formation of byproducts like plazolite, reducing tobermorite content and surface area. These findings provide valuable experimental conditions for effective hydrothermal valorisation of fly ash into functional calcium silicate materials with enhanced textural properties. [13]

Yuan et al. (2023) developed a one-step microwave-assisted hydrothermal method to convert water-washed municipal solid waste incinerated fly ashes into tobermorite, facilitating both the detoxification of hazardous components and the valorisation of fly ash. The process involved treating MSWI-FA with 20 wt.% sodium hydroxide (NaOH) at 260 °C for 3 hours, with quartz sand (Ca/Si=1.1) as a Silica provider. This approach reduced dioxin levels below the HJ 1134–2020 threshold and reduced the leaching concentrations of heavy metals. It also confirmed that above 91% of heavy metals can be stabilized in the hydrothermal product. X-ray diffraction (XRD) analysis confirmed the formation of tobermorite, while scanning electron microscopy (SEM) revealed the development of a mesoporous structure. The main conclusion is that porous tobermorite was synthesized in hydrothermal treatment of WMSWI-FA. The synthesized tobermorite exhibited potential for applications in construction materials and as an adsorbent, highlighting the feasibility of this method for the resource recycling of MSWI-FA.[10]

Qiu et al. (2019) investigated the hydrothermal treatment of municipal solid waste incineration (MSWI) fly ash with a focus on the simultaneous degradation of toxic contaminants and stabilization of heavy metals. Their study demonstrated that microwave-assisted hydrothermal treatment using alkaline additives, particularly sodium hydroxide (NaOH), significantly accelerates the dissolution of silica and aluminium species in fly ash, promoting rapid crystallization of calcium silicate hydrate phases such as tobermorite. Experimental conditions ranged from 150°C to 220°C with treatment times between 1 and 3 hours, revealing that reaction temperature was the most influential factor controlling both contaminant degradation and phase formation, while reaction time played a

secondary but still important role. The use of microwave heating notably reduced reaction times compared to conventional hydrothermal methods, specifically considering the heating rates. The optimal conditions identified for maximizing degradation of polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) and for heavy metal stabilization were 220 °C, 3 hours, and NaOH as the alkaline reagent. Under these conditions, the tobermorite phase crystallized efficiently, contributing to the immobilization of hazardous elements and reducing the toxicity of the treated ash. This dual benefit supports the valorisation of MSWI fly ash by transforming it into a stable, reusable material suitable for incorporation into cementitious products or other industrial applications. The findings highlight that hydrothermal valorisation processes leveraging controlled alkaline media and microwave assistance offer a sustainable pathway to recycle ash residues while mitigating environmental risks. [14]

Hu et al. (2012) explored the hydrothermal treatment of MSWI fly ash with the purpose to reduce its dioxin content. For so, a mixture of ferric sulphate and ferrous sulphate was used as the reactant mixture, and the effect of reaction temperature, pre-treatment by water washing and reactant dosage was assessed. As other authors, one of the main conclusions is that higher reaction temperature is the most influential parameter in the production of mineral structures able to diminish dioxins contamination. [11]

Onnet et al. (2021) reported a study on microwave-assisted hydrothermal synthesis of Zeolite A from bituminous fly ash and demonstrated an efficient valorization pathway for industrial waste through rapid and controlled crystallization. Using sodium hydroxide solutions under microwave irradiation, the process achieved significant reductions in reaction time compared to conventional hydrothermal methods while producing highly crystalline zeolitic materials. The experimental parameters—such as NaOH concentration, microwave power, reaction temperature (~150–180 °C), and time (30–90 minutes)—were optimized to maximize phase purity and surface area. The microwave-assisted approach promoted uniform heating and enhanced nucleation, resulting in well-defined mesoporous structures with increased surface area and pore volume, indicative of effective transformation from amorphous fly ash to crystalline zeolite phases. These findings highlight the potential of microwave-assisted hydrothermal treatment as a sustainable, energy-efficient technology for fly ash valorization, enabling the synthesis of valuable calcium silicate hydrate minerals like tobermorite-related structures with tailored physicochemical properties.[15]

These are some of the most relevant studies found for fly ashes considered as a baseline for the development of this work. Table 1 compiles a summary of additional research works, to show the information gathered for the establishment of the experimental conditions and the expected results.

Table 1. Results of the literature review for biomass fly ash valorisation

Title	Fuel	Fuel properties	Type of reactor	Process temperature	Reagents	Residence time	Reagents dosage	Exp scale	Comments
Facile treatment of municipal solid waste incineration fly ash by hydrothermal method: hazards detoxification and tobermorite synthesis[16]	MSWI-FA	43,49% CaO 11,65% SiO2 0,14% Al2O3 0,46% Cl	Microwave hydrothermal reactor (XH-300PE, Xianghu, China) 2450 MHz and maximum MW power of 1000W	220-260°C	NaOH	2-3 hours	10-20-40-60-80 wt%	5 g mixed with water at L/S ratio of 10 ml/g. 1,54 g quartz sand	NaOH is essential to synthesize tobermorite from MSWI-FA but excessive NaOH has a negative effect on the degradation of dioxins.
Degradation of PCDD/Fs in MSWI fly ash using a microwave-assisted hydrothermal process [17]	MSWI-FA	Dried before and after treating	Microwave apparatus (Sineo MDS-6, China)	150-185-220°	NaOH, Na2HPO4, H2O	1-2-3 hours	reagent dosage was 5 wt% of dried FA	Dried fly ash mixed with reagents and deionized water in a liquid/solid ratio of 3 ml/g	Most efficient path to dioxins degradation: 3 hrs, 260°C using NaOH as reagent
Microwave-assisted hydrothermal treatment with soluble phosphate added for heavy metals solidification in MSWI-FA [18]	MSWI-FA	Dried before experimentation (24 h 105°C)	Microwave apparatus (Sineo MDS-6, China)	Temperature range 100-200°C	NaOH, Na2HPO4, H2O	20 min	0,5-2mol/kg	Dried fly ash mixed with reagents and deionized water in a liquid/solid ratio of 3 ml/g	Most efficient path to heavy metals solidification during hydrothermal process: 200°C, 20 min, 2 mol/kg and 3 ml/g. Using Na2HPO4 as reagent
Stabilization of heavy metals in MSWI-FA in circulating fluidized bed by MW-assisted Hydrothermal treatment with additives [19]	MSWI-FA	Dried before experimentation (24 h 105°C)	Microwave apparatus (Sineo MDS-6, China)	125-150-175-200°C	Na2HPO4 NaH2PO4 H3PO4 FeSO4	10-20 min	0,1-0,2-0,3-0,4 mol/kg	Dried fly ash mixed with reagents and deionized water in a liquid/solid ratio of 3 ml/g	Na2HPO4 is a better additive than NaOH in the hydrothermal process for good solidification of Cd. A higher temperature is needed to make a positive effect on the solidification of Cd and Ni. However, this trend could not be observed for the other

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									heavy metals. The optimized process conditions were 1,5 mol/kg Na2HPO4 2 ml/g L/S ratio 10 min reaction time and 200°C
Hydrothermal decomposition of PCDDs/PCDFs in municipal solid waste incineration fly ash [20]	MSWI-FA	Fly ash contained 600 ng/g of PCDDs and 510 ng/g of PCDFs	60 mL autoclave	225-250-275-300°C	Distilled water NaOH 0,5 N NaOH 1 N NaOH 5 N NaOH 1 N with 10vol% methanol	10 or 20 min		3 g of ash (wet basis) and 27 g solvent	Most effective path for dioxins decompositon: Temp= 300°C time= 20 min Reagent= NaOH 1 N+metOH (100%*) But the results indicated that just alkaline ingredients in solvents accelerated decomposition of PCDDs/PCDFs.
Hydrothermal treatment of municipal solid waste incineration fly ash for dioxin decomposition [21]	MSWI-FA	Total PCCDs/PCDFs content of raw fly ash was 11463 ng/kg and its toxicity equivalents (TEQ) was 628,8 ng/kg	Autoclave produced by Shandong Shuguang Company 3 L	245-290°C	mixture of ferric sulphate and ferrous sulphate in which the ratio of Fe(III)/Fe(II) is 2.		1, 2, 3 wt%	800 g of raw FA and 1600 g of deionized water were mixed at liquid/solid ratio in the range of 2.5-3	Decomposition and destruction of dioxins without reagents were 80,03 and 46,17%. Fe-sulphates increased the yield of decomposition and destruction 92,3% and 89,59% respectively. In the case of temperature effect, yield of destruction and decomposition have higher values with 290°C. Even at 245°C increased 2378-TCDD concentration. Heavy metal concentration of leach was bigger than raw FA
Hydrothermal synthesis of mesoporous tobermorite from fly ash with	**Fly ash (FA)** from a coal-fired power plant in	SiO_2 (~57.1%), Al_2O_3 (~21.4%), CaO (~6.0%), Fe_2O_3 (~5.9%)	Hydrothermal reactor; 1 L autoclave	180-260 °C	CaOH, NaOH	4 hours	20 ml/g		Confirms tobermorite and plazolite phases. Tobermorite synthesized from fly ash via hydrothermal treatment is

enhanced removal performance towards Pb2+ from wastewater	Inner Mongolia, China.								a highly effective, low-cost adsorbent for Pb^{2+} removal from wastewater. Best conditions: 180 °C hydrothermal synthesis for 4 hours.

According to the literature review, some preliminary considerations were identified for a proper design of experiments:

- First, there is a clear research gap on the valorisation of fly ash coming from biomass: very little research was found in this area. This highlights a clear opportunity of finding a new pathway for the valorisation of this residue towards added-value products. It also minimises the environmental impact that they can have after the biomass incineration. Thus, it is considered that a rigorous and analytical work must be undertaken in order to maximise the impact of this new pathway.
- Secondly, the literature review shows that temperature is the most important factor in the production of crystalline structures from ashes. Moreover, the higher the temperature, the higher the crystalline production. Therefore, based on the experience in handling the microwave equipment, the temperature will be maximised.
- Related to the previous point, hydrothermal valorisation by microwave heating improves the efficiency of the process from a thermal and energetic point of view: the structures are generated faster, the energy transfer is more efficient, and the process is therefore shorter.
- It is important for the process to be carried out in a high pH solution. Among the different chemical agents that can contribute to the process, NaOH seems to be the most suitable, due to the Na supply as well as its basic character.
- For the generation of these structures, an external contribution of Si is necessary. This is why it has been decided to add a source of silicon, in our case, silica sand.
- Residence time showed comparatively minor influence on product formation, provided sufficient duration was allowed, if sufficient time is allowed for the generation of these structures.

These results defined the key experimental parameters, which are detailed in Table 2.

Table 2. Experimental conditions of treating incinerated biomass fly ashes

Code	Temperature (°C)	Residence time (min)	% NaOH (wt.%)	Pressure (bar)	Silicon (%wt.)
W2WASH001	175	60	0	40	40
W2WASH002	175	60	30	40	40
W2WASH003	175	60	60	40	40
W2WASH004	200	60	0	40	40
W2WASH005	200	60	30	40	40
W2WASH006	200	60	60	40	40
W2WASH007	225	60	0	40	40
W2WASH008	225	60	30	40	40
W2WASH009	225	60	60	40	40

The residence time of 60 minutes has been considered as the optimal for achieving a compromise between enough residence time for the structures to form, and tests short enough to be able to process them in a single working day. The temperature effect will be assessed considering the maximum temperature achieved in the HTC process developed on D11.1. The NaOH ratio will also

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be assessed (expressed as wt.% with respect to the ash), and the silica quantity has been established as constant throughout all the experiments. This approach will allow us to test the most influential parameters found in literature: temperature and % NaOH.

In parallel to all this review, several companies that incinerate biomass in their processes have been contacted for the supply of ashes. A major company producing electricity from biomass in Spain (both woody and herbaceous biomass) was finally selected as the supplier of this type of material.

3.2. EXPERIMENTAL PROCEDURE

Once the theoretical fundamentals have been established and the strategy for examining the effect of temperature and alkali effect has been determined, the next step in the research was to carry out ash recovery tests. For the experimental trials, a microwave-assisted batch reactor was used (for further information, see the setup description included in the hydrothermal carbonisation section, reported in D11.1). As in this reported work, ethylene glycol has been used as a microwave susceptor, and the reaction solvent was also water. A pressure of 40 bar was initially set, to avoid that water reaches boiling conditions. This pressure was achieved thanks to a nitrogen atmosphere, that also contributed to conduct the reaction in anaerobic conditions.

For the preparation of the experiments, first the established amount of ash (5 grams in all cases) was weighed directly into the reaction vial. Then, 2 grams of silica sand and the calculated amount of water were added. Subsequently, the required amount of NaOH was added to the reaction mixture. The vial was then placed in the rack, which allows up to 3 vials to be fitted, and positioned on the reactor. The reaction conditions, i.e. heating ramps, maximum temperature, residence time, stirring and initial pressure, were programmed. Stirring and residence time were fixed the same for all the experiments developed. The initialisation procedure was then followed according to the instructions of the equipment.

Finally, on completion, the reaction was allowed to cool during 2h and the materials obtained were separated and filtered. Finally, the sample was dried and stored until analysis. The parameters of NaOH dosage and reaction temperature were investigated for synthesizing zeolitic structures and will be further studied for dioxin degradation and stabilizing heavy metals.

3.3. CHARACTERIZATION OF THE RESULTING MATERIALS

Having established the experimental matrix and successfully synthesized the treated ash samples under varied hydrothermal conditions, the next step involved their morphological and compositional characterization. To this end, scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX) was employed to assess the crystallinity, microstructure, and elemental distribution of the resulting materials. The structures presented herein are morphologically inferred until XRD confirms the obtained results.

4. RESULTS AND DISCUSSION

This section presents the results obtained from the hydrothermal treatment of biomass ashes under varying alkaline and thermal conditions. Following the experimental framework outlined in the methodology, nine ash samples (W2WASH001–W2WASH009) were subjected to microwave-assisted hydrothermal processing at different temperatures (175, 200, and 225 °C) and NaOH concentrations (0, 30, and 60 wt.%). The main objective of this analysis is to study how these operational parameters influence the mineralogical transformation of the ash, particularly the formation of calcium silicates hydrates (C–S–H) and zeolitic aluminosilicates.

To this end, high-resolution Scanning Electron Microscopy (SEM) was employed to obtain and examine morphological changes across the different obtained samples, while Energy-Dispersive X-ray Spectroscopy (EDX) provided complementary compositional data, which supports phase identification. Morphological elements, such as fibrous structures, prismatic crystals, polyhedral aggregates, and amorphous gel-like surfaces, were found and interpreted considering literature (e.g., xonotlite, tobermorite, cancrinite, analcime, sodalite), and correlated to the experimental conditions and compositional shifts observed via EDX. It is important to bear in mind that the results presented herein are preliminar – correlations between structural elements and compositional data - and will need to be confirmed with subsequent analytical techniques.

The results are presented in a sample-by-sample basis. Each subsection highlights the key microstructural features, corresponding elemental composition, and inferred mineral phases. The relationship between temperature and NaOH concentration is deeply studied, and how they influence the balance between C–S–H gel formation and zeolite crystallization. SEM images are marked where specific structures are morphologically distinguishable, and the findings are further contextualized within the aim of ash valorization for safe immobilization of inorganics and potential reuse.

4.1. SEM RESULTS

The nine experiments are discussed in three alkaline regimes that cut across the temperature series.

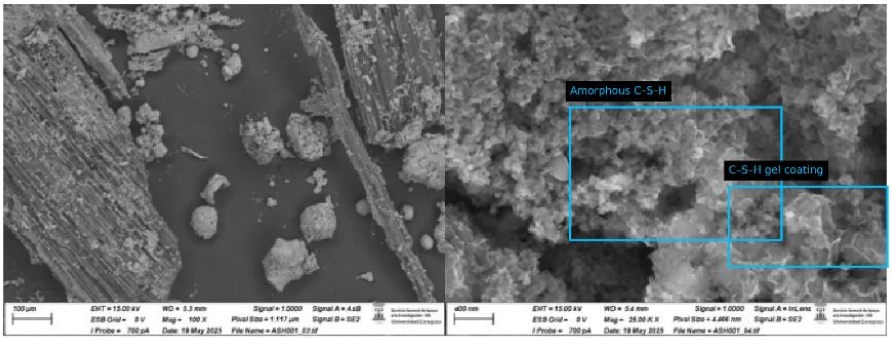
Table 3. Categorization of experiments by alkaline regime

Regime	Samples (T = 175 / 200 / 225 °C)	Dominant phases	Key microstructural trait
Low alkalinity 0 wt. % NaOH	W2WASH001 / 004 / 007	C-S-H → tobermorite → xonotlite	From amorphous gel to dense needle mats
Moderate alkalinity 30 wt. % NaOH	W2WASH002 / 005 / 008	C-S-H + zeolite mix (tobermorite ± analcime ± cancrinite)	Intergrowth of needles and faceted zeolite crystals
High alkalinity 60 wt. % NaOH	W2WASH003 / 006 / 009	Sodalite → analcime / cancrinite	Progressive replacement of Ca-silicates by coarse zeolite aggregates

0 wt.% NaOH – cementitious pathway

At 175 °C (W2WASH001) the ash evolves only into a gel-like calcium silicate hydrate (C-S-H) network with very low crystallinity. Raising the temperature to 200 °C (W2WASH004) drives tobermorite/xonotlite crystallisation, visible as plate-to-needle bundles. At 225 °C (W2WASH007) the system reaches almost pure xonotlite, forming compact mats of interlocked needles that leave little porosity and no zeolitic overgrowth. In short, temperature alone is sufficient to transform an amorphous C-S-H gel into a robust, thermally stable hydrate when alkalinity is kept minimal. These results are depicted in Figure 1.

a.



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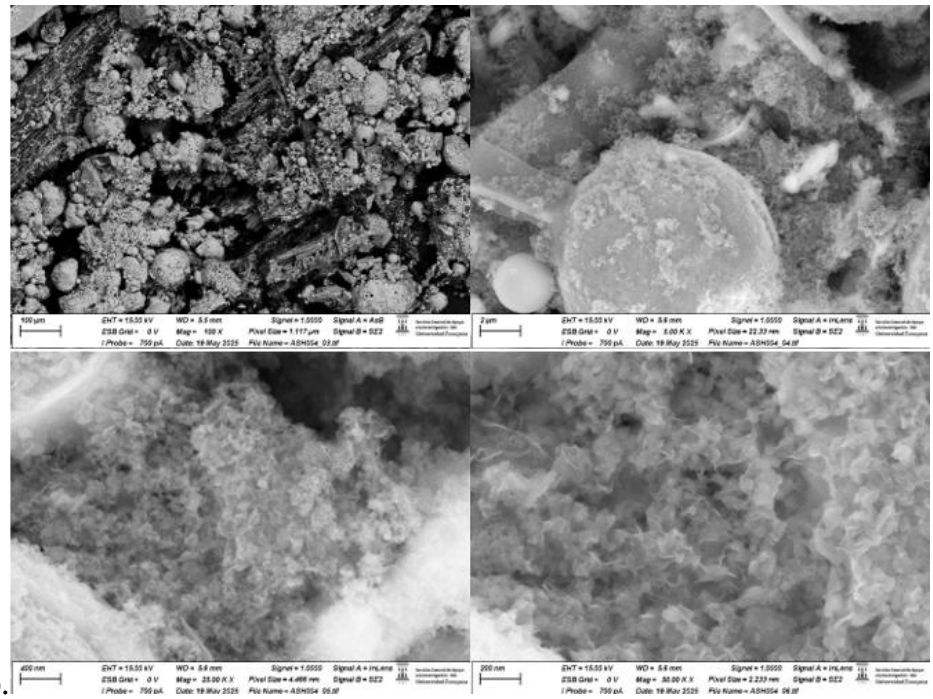
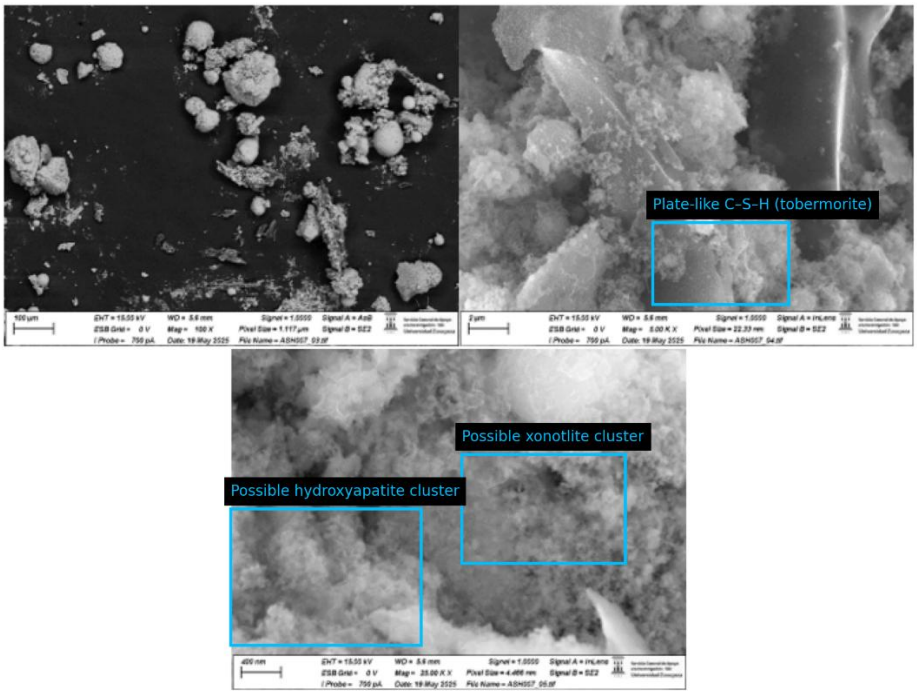


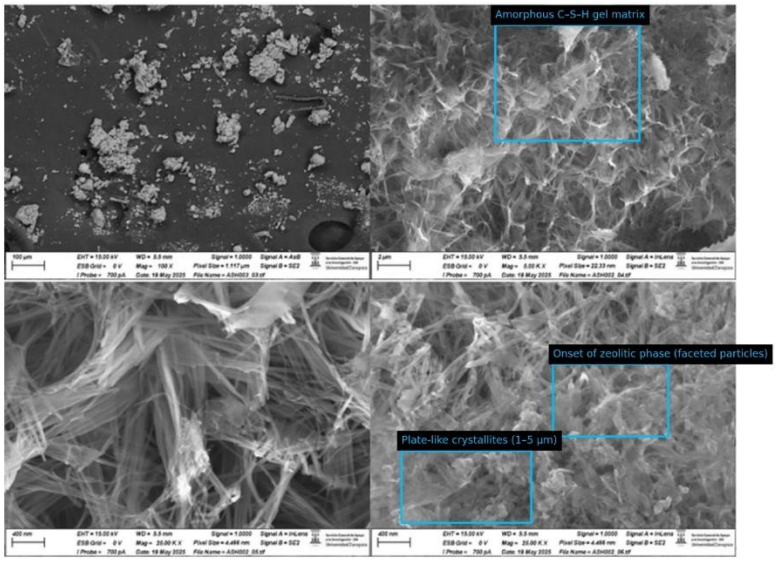


c.

Figure 1. Samples for 0% NaOH tests. a. 175 °C; b. 200 °C; c. 225 °C

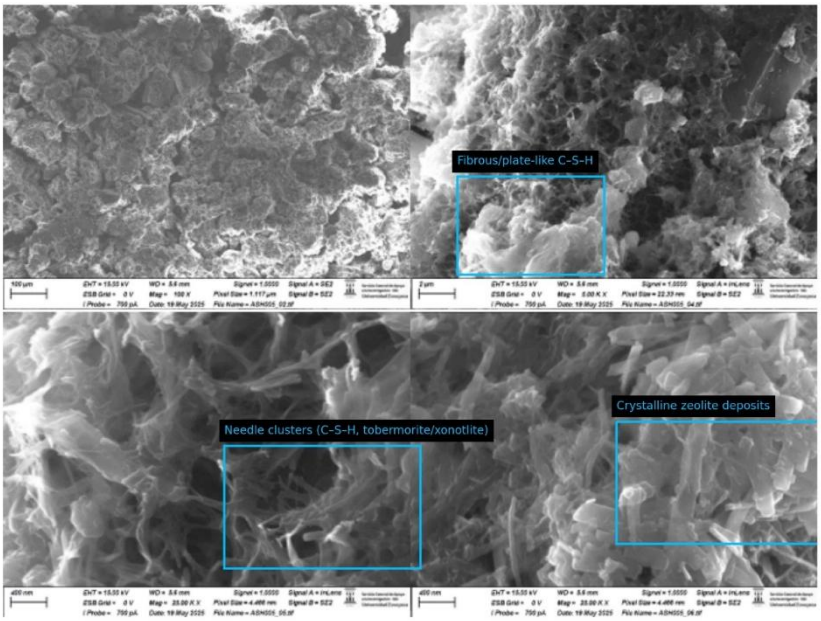
30 wt.% NaOH – hybrid pathway

Moderate alkalinity already seeds zeolite formation at the lowest temperature: W2WASH002 shows incipient sodalite cubes decorating the C-S-H matrix. At 200 °C (W2WASH005) a composite texture appears—tobermorite needles show a scaffold that includes analcime and sodalite crystals. Pushing to 225 °C (W2WASH008) amplifies this synergy: xonotlite bundles coexist with large cancrinite/analcime prisms, suggesting near-optimum conditions for simultaneous immobilisation and mechanical performance. Thus, moderate NaOH balances Ca- and Na-silicate pathways, yielding multifunctional products rather than favouring a single-phase family. These results can be observed in Figure 2.



a.

b.



c.

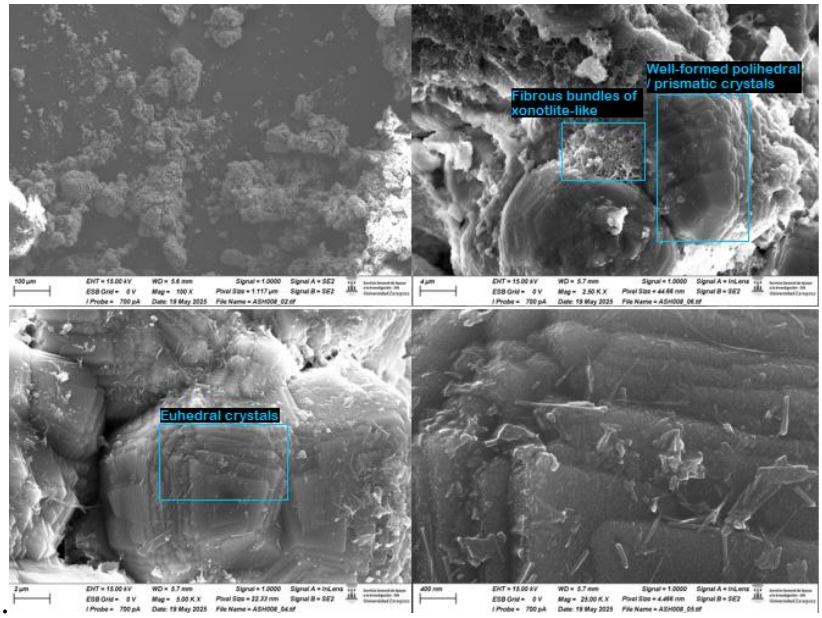
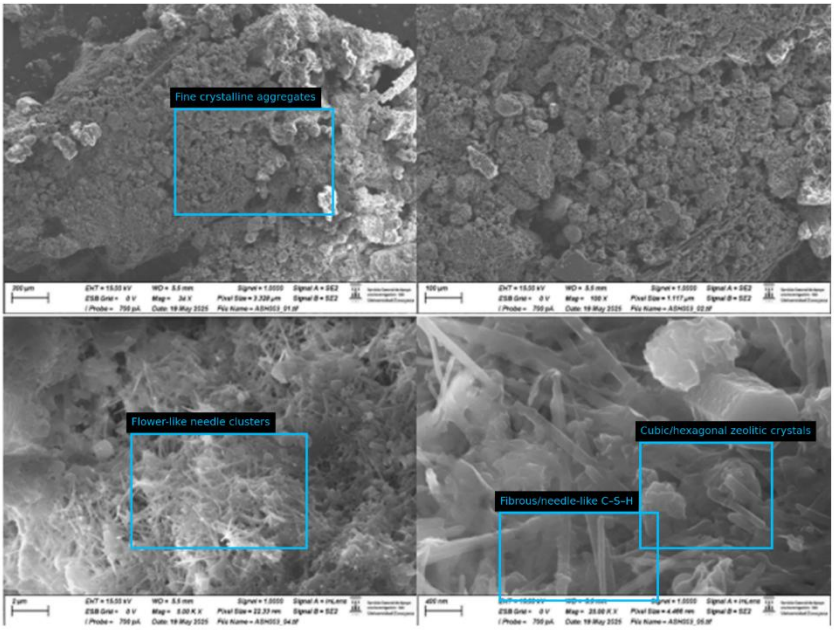


Figure 2. Samples for 30% NaOH tests. a. 175 ºC; b. 200 ºC; c. 225 ºC

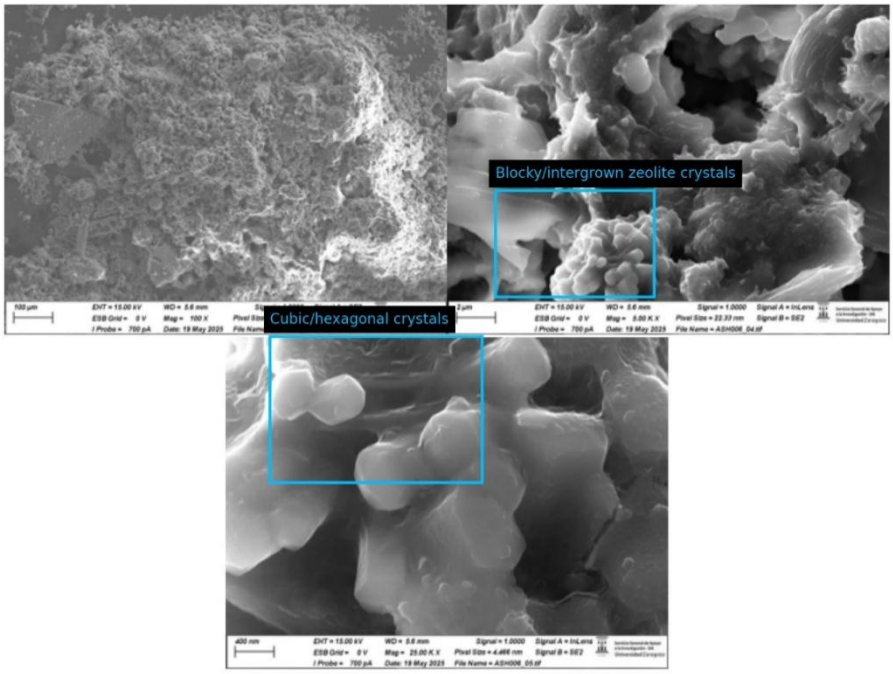
60 wt.% NaOH – zeolitic pathway

With strong alkalinity, even 175 °C (W2WASH003) produces a porous foam dominated by sodalite/cancrinite micro-crystals. At 200 °C (W2WASH006) the Ca supply is largely consumed; the solid converts into dense polyhedral analcime and cancrinite aggregates with remaining C-S-H. Finally, 225 °C (W2WASH009) yields a pure zeolitic matrix of analcime crystals, representing full ash conversion to aluminosilicate frameworks. Hence, high NaOH drives rapid dissolution of Si/Al and shifts the equilibrium toward zeolitisation, progressively suppressing calcium silicates as temperature grows. Figure 3 shows the descripted structures.

a.



b.



c.

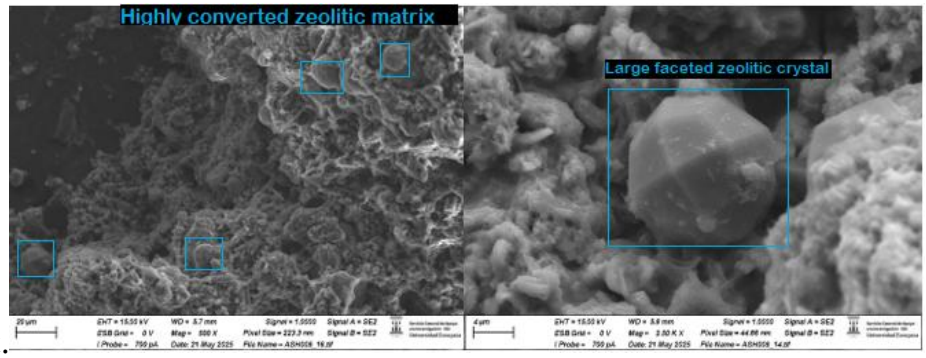


Figure 3. Samples for 60% NaOH tests. a. 175 °C; b. 200 °C; c. 225 °C

4.2. Effect of Temperature

Temperature played a pivotal role in the type and crystallinity of the mineral structures formed during the applied hydrothermal treatment. At lower temperatures, the ash suffered partial transformations, enhancing the creation of amorphous or low-grade crystalline calcium silicate hydrate (C–S–H), along with some zeolitic structures, which seem to correspond to analcime. When the temperature raised, the trend grew towards the formation of more crystalline and stable phases, the generation of tobermorite and xonotlite became plausible, as confirmed by SEM morphology.

The high-temperature samples showed dense needle-like networks, which is an indicative of more ordered C–S–H structures. In some cases, the substitution of tobermorite by xonotlite was also appreciable. The shift in phase stability and crystallization is consistent with known thermal requirements of these phases, with higher temperatures promoting crystallinity, mineral purity, and stability. Moreover, high temperatures appear to facilitate the complete dissolution and reorganization of ash components, accelerating the precipitation of calcium-derivate structures and potentially enhancing immobilization efficiency for harmful elements.

4.3. Effect of NaOH concentration

The concentration of NaOH significantly influenced the pathways of mineral formation, particularly in shaping the balance between C–S–H and zeolitic phases. At low alkaline environments, the environment limits the dissolution of silica and alumina, and resulting predominantly in C–S–H structures with limited crystal growth. At moderate alkalinity, the enhanced dissolution of Si and Al facilitated the simultaneous development of tobermorite and zeolites such as analcime, suggesting an optimal condition for the co-formation of both cementitious and absorptive phases. However, at highest alkalinities, zeolite formation became more dominant, with SEM–EDX confirming abundant sodium–aluminium–silicate crystallization and a relative suppression of C–S–H growth, likely due to competition for silicate species and high ionic strength inhibiting Ca–Si interactions. The high alkalinity also promoted the formation of chloride-incorporating phases like cancrinite, contributing to better chemical fixation of halogens.

Overall, NaOH concentration dictates the mineral equilibrium: moderate concentrations support multifunctional phase co-precipitation, while high levels shift the balance towards zeolitization and alkali incorporation.

Finally, Table 4 summarizes the observations and structural differences observed for all the samples:

Table 4. Summary of the results of the experimental campaign

Sample Code	Main Identified Phases	Morphology (SEM)	Interpretation / Immobilization Potential
W2WASH001	Amorphous C–S–H gel	Gel-like, irregular aggregates	Early-stage Ca–Si hydrate formation. Low crystallinity. Some encapsulations of inorganics possible.

W2WASH002	C–S–H initial sodalite	Fine cubic particles on gel	Onset of zeolitization. Improved surface area for cation binding.
W2WASH003	Sodalite + Cancrinite (minor)	Porous network, fine crystals	Zeolitic structure dominates. High Na content. Good potential for ion exchange and heavy metal sorption.
W2WASH004	Tobermorite + C–S–H	Needles, plates, aggregates	Well-formed C–S–H. Suitable for structural reuse or cementitious applications. Moderate heavy metal retention.
W2WASH005	Tobermorite + Analcime + Sodalite	Mixed needles and crystals	Composite structure. High multifunctionality (strength + sorption).
W2WASH006	Analcime + Cancrinite	Polyhedral and cubic crystals	Zeolite-dominated. Strong immobilization potential, especially for cations.
W2WASH007	Xonotlite (C–S–H)	Dense needle mats	Thermally stable hydrate. Strong encapsulation. Minimal leachability.
W2WASH008	Xonotlite + Cancrinite + Analcime	Fibers + hexagonal prisms	Balanced phase mixture. Excellent candidate for immobilization and mechanical use.
W2WASH009	Analcime (dominant) + Cancrinite	Large zeolite crystals	Pure zeolitic matrix. Strong ion-exchange potential, minimal Ca phases.

5. CONCLUSIONS

The hydrothermal treatment of the incinerated biomass fly ashes successfully converted raw waste ash into a material enriched with beneficial mineral phases, while substantially reducing leachable contaminants:

- Significant amounts of tobermorite under moderate hydrothermal conditions seem to be generated, upon XRD confirmation. At more extreme conditions, xonotlite (a crystalline and thermally stable C–S–H) was also formed. The presence of these C–S–H phases is desirable, as they can contribute to mechanical strength and chemical stability if the material is used as a cement or concrete additive. Consequently, zeolitic phases like analcime or cancrinite were formed thanks to the ash's aluminosilicate components, especially in the tests with high alkalinity. These zeolites can immobilize alkalis and potentially serve environmental remediation roles.
- Phosphorus immobilization: The process also immobilized other important elements. Phosphorus coming from the ashes precipitated as apatite. This converts phosphorus into a stable and non-leaching form (and one that could even be beneficial as a slow-release fertilizer if the material were ever used agriculturally).
- Microstructural and chemical stability: The ashes exhibit a consolidated microstructure with formed crystalline networks (tobermorite/xonotlite needles and zeolite crystals) binding the matrix. This indicates a greater structural integrity compared to the raw ash. Chemically, toxic components (like heavy metals if present, chlorides, etc.) seem to be washed out or fixed into mineral structures, suggesting that the hydrothermal process stabilizes the ash and reduces its environmental danger.
- These findings confirm hydrothermal treatment as an effective valorisation pathwayfor biomass combustion ashes. By adjusting treatment parameters (temperature, time, alkalinity), the product's mineral composition can be tuned. For instance, if the goal is maximum activity for cement, conditions can be chosen to favor tobermorite formation. If the goal is to create a sorbent material, conditions can vary towards more zeolite formation. In all cases, the treated ash shows a marked improvement over the raw ash in terms of handling and usefulness.
- Alignment with sustainable practices: The hydrothermal strategy works at relatively low temperatures and uses water and an alkali solution, making it energy-efficient and with low emissions. Implementing such treatments at scale could help biomass power plants and industries reduce waste disposal costs and environmental impact, while producing secondary products that have economic value (be it as construction material additives, soil enhancers, or pollution control media).
- Moderate alkalinity (30 wt.%) at high temperature emerges as the "sweet spot" where a C-S-H skeleton and high-surface-area zeolites co-form, combining structural strength with ion-exchange capacity.

In conclusion, the comprehensive analysis of samples W2WASH001–W2WASH009 demonstrates that through hydrothermal treatment, biomass ash can be cleaned of undesirable soluble components and simultaneously converted into a composite of cementitious and zeolitic

minerals. The treated ash is thus rendered suitable for beneficial reuse. These results are in excellent agreement with and extend the findings of previous research on ash hydrothermal conversion, underscoring the potential of this method to contribute to sustainable waste management and materials innovation.

Future work may involve testing the performance of this treated ash in real cement mixes and evaluating long-term durability, but the present study provides a strong foundation (both literally and figuratively) for the effective recycling of biomass ash into useful products.

5.1. NEXT STEPS

To fully elucidate the material's applicability and safety, several additional analyses are essential. First, further structural characterization techniques such as X-ray diffraction (XRD) and transmission electron microscopy (TEM) should be conducted. These will allow to quantify crystallinity and analyse internal microstructures of the generated crystals. Transmission electron microscopy (TEM) will help to visualize the internal structure of materials at nanoscale, and should be employed to quantify the crystallinity, phase purity, and lattice features of the synthesized structures. Complementary techniques like FTIR and solid-state NMR can help confirm functional groups and structures in C–S–H and zeolites.

Second, leaching tests following standardized protocols must be conducted to assess the environmental stability of immobilized elements, especially heavy metals like Pb, Zn, and Cu. This will determine the potential for safe reuse in construction or soil applications.

Third, to evaluate the ashes' role in organic pollutant mitigation, targeted dioxin and PCB analyses should be conducted, using GC–MS techniques. This will confirm whether the alkaline hydrothermal environment degrades or adsorbs these compounds during treatment. If confirmed, this dual-purpose valorisation (mineral synthesis + detoxification) could position hydrothermal ash treatment as a sustainable remediation technology.

With all these, several scientific peer-reviewed publications are expected from the contents explored in this report, which will ultimately target the disseminations of results within the scientific community and improving the state-of-the-art of novel environmentally friendly energy efficient approaches such microwave-assisted innovative technologies.

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