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**Controlling Phase Transformation for the Design
of Phosphorus Recovery Processes
from Secondary Inorganic Resources**

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Abstract – Italiano

Il fosforo (P) è un elemento essenziale per la vita e rappresenta una risorsa strategica per numerosi settori industriali, in particolare per la produzione di fertilizzanti e, più recentemente, per applicazioni avanzate quali i materiali per batterie. Tuttavia, la sua disponibilità è strettamente legata a giacimenti naturali limitati e distribuiti in maniera geopoliticamente non uniforme, rendendo il fosforo una materia prima critica (Critical Raw Material, CRM) per l'Unione Europea. In questo contesto, il recupero di fosforo da risorse secondarie si configura come una necessità sempre più urgente per garantire la sicurezza degli approvvigionamenti e promuovere modelli di economia circolare.

La presente tesi si inserisce in questo scenario con l'obiettivo di approfondire i meccanismi che governano la trasformazione e la recuperabilità del fosforo in matrici inorganiche complesse, adottando un approccio basato sulla caratterizzazione mineralogica e sul controllo delle trasformazioni di fase. A differenza degli approcci tradizionali, prevalentemente focalizzati sull'ottimizzazione delle rese di estrazione, questo lavoro pone al centro dell'analisi la natura cristallina delle fasi contenenti fosforo e il loro ruolo nella determinazione della reattività e della solubilità.

Sono state selezionate due tipologie rappresentative di risorse secondarie: le ceneri da incenerimento di fanghi di depurazione (sewage sludge ash, SSA) e la black mass derivante da batterie esauste al litio-ferro-fosfato (LFP). Questi materiali, seppur differenti per origine e composizione, presentano una problematica comune: la presenza del fosforo in fasi cristalline stabili e scarsamente solubili, quali fosfati di calcio, ferro e alluminio nel caso delle SSA, e la struttura olivinica del LiFePO_4 nelle batterie LFP. Tali caratteristiche limitano fortemente l'efficacia dei processi di recupero basati esclusivamente su trattamenti di lisciviazione.

Nel primo caso, relativo alle SSA, è stato indagato l'effetto della carbonatazione in ambiente acquoso come pretrattamento volto a ridurre il pH delle ceneri in soluzione e a favorire la successiva estrazione del fosforo mediante lisciviazione acida. I risultati hanno evidenziato come la formazione di fasi carbonatiche contribuisca a una riduzione del pH ma non ad una maggiore estrazione del fosforo. Successivamente, sono stati studiati trattamenti termochimici assistiti da microonde in presenza di additivi alcalini (NaHCO_3 e KHCO_3), con l'obiettivo di indurre trasformazioni di fase controllate. Tali trattamenti hanno portato alla formazione di nuovi fosfati più reattivi, come NaCaPO_4 e KCaPO_4 , evidenziando al contempo differenze significative tra gli additivi utilizzati in termini di redistribuzione del fosforo e comportamento in lisciviazione.

Nel secondo caso, relativo alla black mass da batterie LFP, l'approccio termochimico assistito da microonde è stato utilizzato per trasformare la struttura cristallina catodica LiFePO_4 in nuove fasi. In presenza di NaHCO_3 in due diverse quantità, il trattamento ha favorito la formazione di fasi cristalline

fosfatiche solubili o insolubili e costituiti da ferro-sodio-litio. I risultati dimostrano la possibilità di recuperare simultaneamente fosforo e litio, trasformando un rifiuto a basso valore in una potenziale risorsa per applicazioni future. Inoltre, le trasformazioni indotte suggeriscono la possibilità di ottenere materiali a struttura aperta, come quelli di tipo NASICON, con potenziali applicazioni nel campo dell'elettrochimica.

L'intero lavoro sperimentale è stato supportato da un'analisi approfondita mediante tecniche avanzate di caratterizzazione, tra cui la diffrazione a raggi X con analisi quantitativa di fase (XRPD-QPA), la microscopia elettronica a scansione con microanalisi (SEM-EDS) e l'analisi chimica dei lisciviati tramite ICP-OES e TXRF. Questo approccio integrato ha permesso di correlare in modo sistematico la composizione di fase, la microstruttura e il comportamento in lisciviazione, fornendo una comprensione dettagliata dei meccanismi che regolano la trasformazione e la mobilità del fosforo.

Nel complesso, la tesi dimostra come il controllo delle trasformazioni di fase rappresenti un elemento chiave per superare le limitazioni dei processi convenzionali e migliorare l'efficienza del recupero del fosforo da matrici secondarie complesse. I risultati ottenuti contribuiscono a colmare il divario di conoscenza sui meccanismi microscopici di redistribuzione del fosforo durante i trattamenti termochimici e offrono nuove prospettive per lo sviluppo di strategie sostenibili e innovative per la valorizzazione delle risorse secondarie.

Abstract - English

Phosphorus (P) is an essential element for life and a strategic resource for several industrial sectors, particularly for fertilizer production and, more recently, for advanced applications such as battery materials. However, its availability is closely linked to limited natural deposits that are unevenly distributed from a geopolitical perspective, making phosphorus a Critical Raw Material (CRM) for the European Union. In this context, phosphorus recovery from secondary resources has become an increasingly urgent necessity to ensure supply security and promote circular economy models.

This thesis is framed within this scenario and aims to investigate the mechanisms governing phosphorus transformation and recoverability in complex inorganic matrices through an approach based on mineralogical characterisation and phase transformation control. Unlike traditional approaches, which are mainly focused on optimizing extraction yields, this work places the crystalline nature of phosphorus-bearing phases and their role in determining reactivity and solubility at the core of the analysis.

Two representative types of secondary resources were selected: sewage sludge ash (SSA) derived from mono-incineration processes and black mass obtained from spent lithium iron phosphate (LFP) batteries. Although these materials differ in origin and composition, they share a common challenge: the occurrence of phosphorus in stable and poorly soluble crystalline phases, such as calcium, iron, and aluminium phosphates in SSA, and the olivine crystal structure of LiFePO_4 in LFP batteries. These characteristics strongly limit the effectiveness of recovery processes based solely on leaching treatments.

In the first case, concerning SSA, the effect of aqueous carbonation as a pre-treatment was investigated in order to lower the pH of the ash suspension and promote subsequent phosphorus extraction through acid leaching. The results showed that the formation of carbonate phases contributed to a reduction in pH but did not lead to enhanced phosphorus extraction. Subsequently, microwave-assisted thermochemical treatments in the presence of alkaline additives (NaHCO_3 and KHCO_3) were studied with the aim of inducing controlled phase transformations. These treatments promoted the formation of new and more reactive phosphate phases, such as NaCaPO_4 and KCaPO_4 , while also highlighting significant differences between the additives in terms of phosphorus redistribution and leaching behaviour.

In the second case, concerning the LFP battery black mass, the microwave-assisted thermochemical approach was employed to transform the crystalline cathodic structure of LiFePO_4 into new phases. In the presence of NaHCO_3 at two different dosages, the treatment promoted the formation of soluble and insoluble phosphate crystalline phases composed of iron, sodium, and lithium. The results demonstrate the possibility of simultaneously recovering phosphorus and lithium, thereby

transforming a low-value waste into a potential resource for future applications. Furthermore, the induced transformations suggest the possible formation of open-framework materials, such as NASICON-type structures, with potential applications in the field of electrochemistry.

The entire experimental work was supported by an extensive characterisation campaign using advanced analytical techniques, including X-ray powder diffraction with quantitative phase analysis (XRPD-QPA), scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS), and chemical analysis of leachates by ICP-OES and TXRF. This integrated approach enabled the systematic correlation between phase composition, microstructure, and leaching behaviour, providing a detailed understanding of the mechanisms governing phosphorus transformation and mobility.

Overall, this thesis demonstrates that phase transformation control represents a key strategy for overcoming the limitations of conventional recovery processes and improving phosphorus recovery efficiency from complex secondary matrices. The obtained results contribute to bridging the knowledge gap concerning the microscopic mechanisms of phosphorus redistribution during thermochemical treatments and provide new perspectives for the development of sustainable and innovative strategies for secondary resource valorisation.

Abbreviation	Definition
BM	Black Mass
CA	Citric Acid
CRM	Critical Raw Material
EDS	Energy Dispersive Spectroscopy
EU	European Union
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
LIB	Lithium-Ion Battery
LCO	Lithium Cobalt Oxide
LFP	Lithium Iron Phosphate
LMO	Lithium Manganese Oxide
MW	Microwave
NAC	Neutral Ammonium Citrate
NCA	Lithium Nickel Cobalt Aluminium Oxide
NCM	Lithium Nickel Cobalt Manganese Oxide
NASICON	Sodium Super Ionic Conductor
P	Phosphorus
PR	Phosphate Rock
QPA	Quantitative Phase Analysis
SEM	Scanning Electron Microscopy
SS	Sewage Sludge
SSA	Sewage Sludge Ash
TXRF	Total Reflection X-ray Fluorescence
UV–Vis	Ultraviolet–Visible Spectroscopy
WWTP	Wastewater Treatment Plant
XRD	X-ray Diffraction
XRPD	X-ray Powder Diffraction
XRPD-QPA	X-ray Powder Diffraction – Quantitative Phase Analysis

1. Natural Phosphorus (P) Deposits and Secondary P-sources

1.1 Phosphorus Deposits Formation, Global Presence, and Extraction

The primary natural sources of phosphorus (P) are phosphate rocks (PR), mainly represented by the sedimentary (95% of the total reserves) mineral deposits. The other 5% is constituted by magmatic PR found in carbonatitic or alkaline complexes and associated with subduction or rifting areas, thanks to a concentration of P in the magma and to an early crystallisation of it in the form of apatite (mainly fluorine apatite) $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$ close to the liquidus temperature. The formation of P minerals is influenced by the temperature of the magma and the concentration of SiO_2 , CaO , and Al_2O_3 . These are high-purity PR rocks containing up to 5-15% of P_2O_5 and a lower content of contaminants compared to sedimentary PR, including uranium (U), thorium (Th), and rare earth elements (REEs) frequently associated with carbonatitic complexes [1]. The formation of sedimentary PR, instead, is related to marine environments following biogeochemical processes related to the P cycle. The formation is due to the upwelling of enriched P oceanic waters, where P is dissolved mainly in the PO_4^{3-} , to shallower areas as continental platforms or epicontinental seas. P is here absorbed by the phytoplankton and algae, becoming part of the organic matter and promoting biomass proliferation. When these marine organisms die, they accumulate on the seafloor, where aerobic and anaerobic bacteria degrade the organic matter, releasing PO_4^{3-} that permeates the sediment pores. Having a high concentration of P and of Ca^{2+} and F^- in the pores, a high alkalinity (high values of pH) and sub-oxic or anoxic conditions, the precipitation of phosphatic minerals can occur. A mineral with complex chemistry is formed [2], which is called francolite $\text{Ca}_{10-a-b}\text{Na}_a\text{Mg}_b(\text{PO}_4)_{6-x}(\text{CO}_3)_x\text{F}_{0.4x}\text{F}_2$ [3] a variety of apatite containing a CO_3 group. Once formed, francolite must accumulate and preserve to form an economic deposit. This is done through diagenetic and sedimentological processes through which francolite can lose the carbonate group and form common and pure apatite [1]. Further, different PR rocks, also called phosphorites, can be formed, containing laminated or granular deposits, often concentrated along key stratigraphic surfaces. These deposits can contain 10% to 35% of P_2O_5 , with the most interesting ones, the granular deposits, usually containing 30-35% of P_2O_5 . The higher content of P is, however, accompanied by a higher concentration of contaminants such as U and REEs, up to 3000 mg/kg and 18000 mg/kg, respectively [1].

The most significant PR deposits are located in Northern Africa, the Middle East, China, and the United States (Figure 1), with Morocco alone accounting for over 70% of global reserves. Total worldwide phosphate rock resources are estimated to exceed 300 billion tons. As illustrated in Figure 2, China leads in phosphate mining and processing with a production of 35-90 million tons only in

2023, followed by Morocco, Russia, and USA [4]. These countries have sedimentary type deposits on their territory, and where we find those of the igneous type (purely in south-eastern Africa and Brazil), production is nil or less intense.

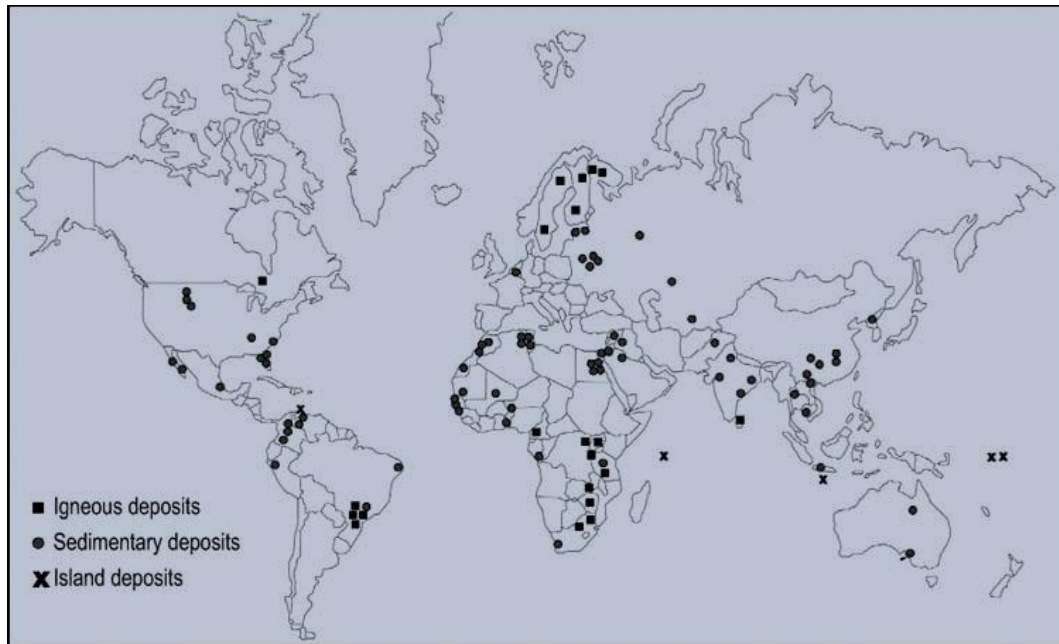


Figure 1. FAO / FAO document represents major extractive deposits (sedimentary, igneous) of PR rocks [5].

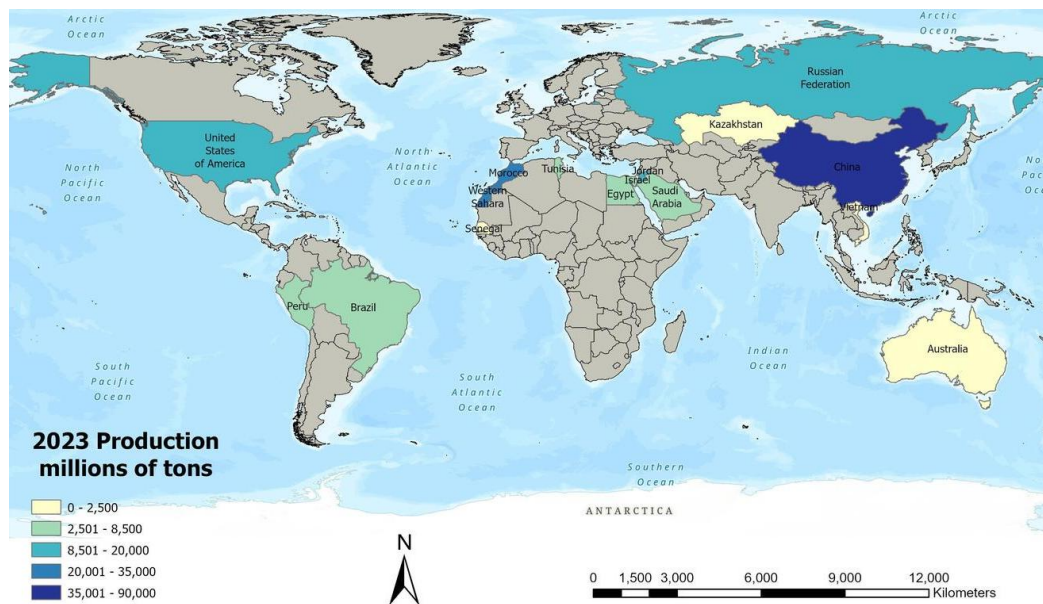


Figure 2. World production of phosphate rock in 2023, expressed in millions of tons. The main producers are China, Morocco, the United States, and Russia. The map shows the geographical distribution of production, with a strong dominance of the Asian and North African areas. Source: [6].

1.1.1 Major Phosphorus Processes and Uses, and Related Environmental Issues

As explained in the previous chapter, PRs are different, and the sedimentary ones are the primary source of P due to their abundance on the continental crust and the easiest access and processability. The main use of phosphorus extracted from sedimentary deposits is the production of phosphate fertilizers. Phosphate fertilizers are therefore widely used in agriculture to improve crop yields and ensure global food security. These fertilizers are obtained by treating sedimentary phosphates with acids, mainly sulfuric acid (H_2SO_4) and nitric acid (HNO_3) (Figure 3).

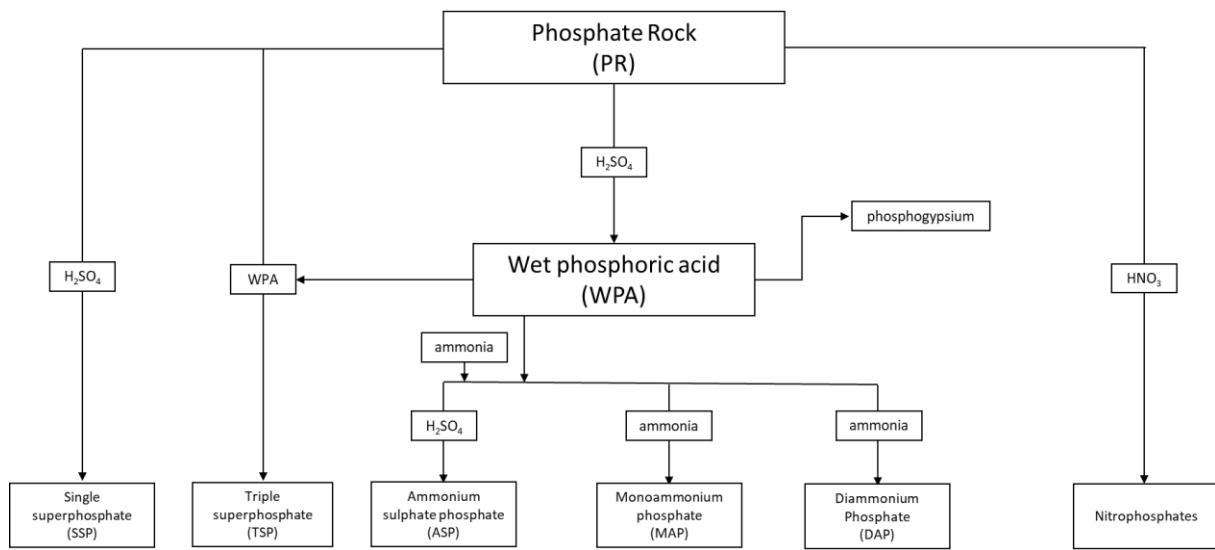
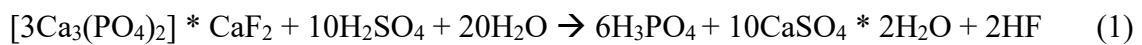


Figure 3. Fertilizer production from PR using H_2SO_4 or HNO_3 [7].

The production of phosphoric acid (H_3PO_4) and the addition of different amounts of ammonia are the fundamental step in the formulation of various types of fertilizers (Figure 3). Following the H_2SO_4 leach, H_3PO_4 is released in the solution according to the reaction (1):



The by-product of this process is the so-called phosphogypsum (PG) that poses significant challenges related to the landfilled stockpiles that have a negative impact on the surrounding land, water, and air, originating chemical and radioactive contamination [8]. Worldwide, only 15% of the PG is recycled, with an estimated yearly production of 100-280 Mt.

Phosphorus derived from sedimentary deposits also plays a key role in the chemical industry. Phosphoric acid can be used for industrial products, including detergents, food additives, preservatives, and even lithium-iron-phosphate (LFP) batteries. For example, phosphates are often used in detergents to improve the effectiveness of washing, although in recent years their use has been reduced in some countries due to environmental concerns about water eutrophication [9].

Phosphorus extracted from these deposits is also used in animal feed. Phosphates are important supplements in animal feed to ensure that domestic and farm animals receive the proper mineral intake necessary for their growth and health [10].

Finally, in the last 30 years, P extracted from PR has also been directed to the production of LFP batteries. PRs can be processed to obtain 3 different sources of P for the LFP battery production: H_3PO_4 , which is widely used due to the lower cost, ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), and FePO_4 , which can be used as a source of both P and Fe. The $\text{NH}_4\text{H}_2\text{PO}_4$ precursor is the most difficult to handle; while relatively stable when exposed to air, it can undergo slight decomposition at temperatures above 100 °C and is highly hygroscopic. This necessitates either immediate use after opening or re-drying before storage. Moreover, during the reaction, it releases ammonia, a potentially harmful compound for the environment, which is typically managed by filtering and absorbing the exhaust gases using an acidic solution [11]. The environmental issues, in this case, are linked mainly to the end-of-life management; If LFP spent batteries are not properly handled, they can lead to environmental degradation and also to the irreversible depletion of valuable and finite natural resources, as both lithium (Li) and P are listed as critical raw materials.

In summary, sedimentary phosphate deposits are the primary source of phosphorus used in multiple sectors, with agriculture as the main recipient, followed by the chemical industry and animal feed. Their importance is such that the sustainable management of these resources is critical to ensuring the future availability of this essential element for life.

1.2 Phosphorus as a Critical Raw Material (CRM) in the European Union Framework

Phosphorus is a naturally occurring chemical element found in various forms throughout the life cycles of all living organisms. It plays a vital role in numerous biochemical processes, including those involving genetic material (DNA and RNA), energy transfer through the adenosine tri/diphosphate (ATP–ADP) cycle, and the structural integrity of cell membranes via phospholipids. Additionally, phosphorus is the second major component of the human body, mainly located in bones and teeth, where it exists in the crystalline form of hydroxyapatite [12]. As previously stated, P is also fundamental to ensure food security all around the world being one of the major nutrients in the fertilizer field, along with nitrogen (N) and potassium (K). According to the Food and Agriculture Organization of the United Nations (FAO). Further, in 2022, the global phosphorus supply, quantified as P_2O_5 , was projected at 52,066 kilotons, exceeding the estimated global demand for fertilizer-grade P_2O_5 , which stood at 49,096 kilotons [13]. In 2018, inorganic phosphorus (P) fertilizer consumption in Europe totalled approximately 1.13 million tonnes [16], with Turkey, France, Spain, Poland, Italy,

Germany, Romania, the United Kingdom, and Hungary each exceeding an annual usage of 50,000 tonnes.

Furthermore, P_2O_5 consumption in the fertilizer sector experienced an estimated year-on-year increase of 7% during the 2020–2021 crop year [4]. In addition, the world P_2O_5 consumption for fertilizer production is increased during the past years, from 2020 to 2021 of about the 7%.

The PR extraction in the previous 25 years has also increased deeply and almost doubled (Figure 4) and is mostly dominated by 5 countries (Figure 5). The PRs, as oil, is considered a non-renewable resource

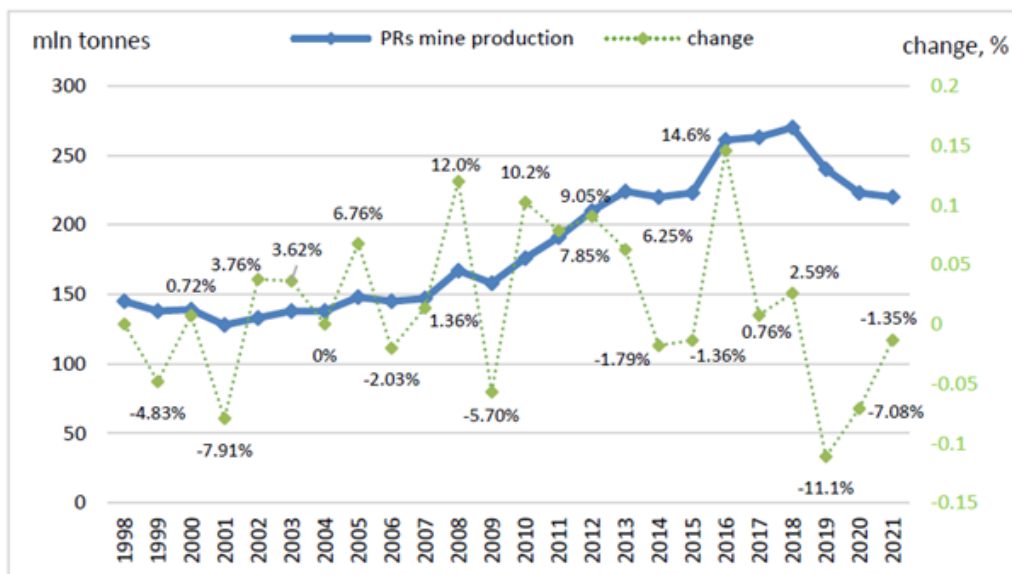


Figure 4. Phosphate rock mine production in the last 25 years [7].

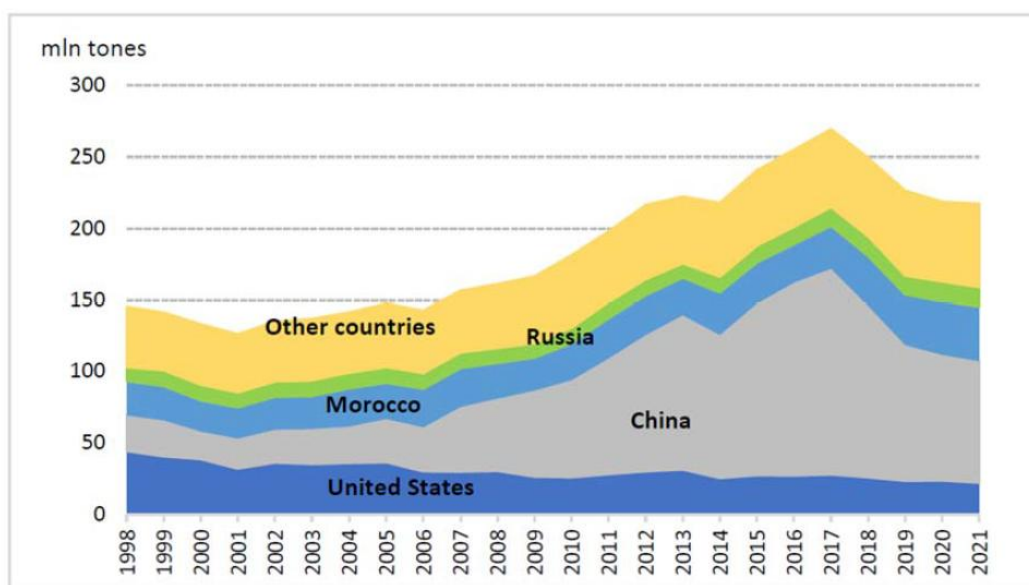


Figure 5. Phosphate rocks mining by country [7].

Another factor to be taken into consideration is the distribution of P and PR rocks around the world (Figure 1), which is geopolitically unfavourable, especially for organizations such as the EU, where there is no extraction but only import of the raw material or product already developed and processed. Compared to other regions globally, the European Union faces a heightened challenge regarding phosphorus (P) scarcity, primarily due to the uneven geographical distribution of phosphate reserves and the dominance of a few countries in global trade. In recognition of this vulnerability, the European Commission has included elemental P in its triennially updated list of Critical Raw Materials (CRMs) since 2017 and PR since 2014 [14]. Consequently, the global issue of phosphorus supply is of particular urgency for the EU, where P is already officially designated as a critical raw material, underscoring the need for alternative sources and sustainable management strategies. To mitigate dependency on depleting resources, the development and implementation of innovative and sustainable technologies are essential, similar to ongoing efforts concerning lithium (vital for rechargeable batteries and the energy transition) and bauxite (the primary ore for aluminium production), both of which were newly classified as CRMs in the 2020 EU report. According to the EU CRM 2023 assessment, the EU import reliance for phosphate rock extraction reaches approximately 82%, while elemental phosphorus processing is characterised by a 100% import reliance. Globally, phosphate rock extraction is dominated by China (44%), followed by Morocco (14%), the United States (10%) and Russia (7%). In terms of EU supply, Morocco represents the main phosphate rock supplier (27%), followed by Russia (24%), Finland (17%), and Algeria (10%). Furthermore, phosphate rock is predominantly used for fertilizer production (86%), while smaller fractions are employed in animal feed applications (10%) and in detergents, chemicals, and food additives (4%). These data further highlight the strategic importance of developing phosphorus recovery routes from secondary resources within a circular economy perspective.

1.3 EU Acts and Plans on Circularity and Secondary P-sources

The depletion of natural resources is an increasingly critical issue, influencing not only current material procurement strategies but also shaping future policy decisions in light of environmental impacts and global ecological shifts. In its Circular Economy Action Plan, adopted on 11 March 2020 [15], The European Commission advocates for the diversification of raw material sources, including the utilization of sustainable biomass. This initiative aims to minimize greenhouse gas (GHG) emissions and reduce the volume of waste sent to landfills, recognizing the pivotal role biomass will play in the advancement of renewable and sustainable energy systems.

Another important step towards the end-of-waste was done with the EU Battery Regulation (2023/1542), which is effective from August 18, 2023, and marks a key step toward establishing a circular economy for batteries within the European Union. By setting legally binding requirements across the entire battery life cycle, from design and production to end-of-life management, the regulation aims to minimise environmental impact, enhance resource efficiency, and ensure the responsible use and recovery of critical raw materials. It reflects the EU's commitment to building a sustainable battery value chain that supports climate neutrality and reduces dependency on external supply sources [16]. According to the European Battery Regulation (2023/1542), recycling efficiency targets for lithium-based batteries have been set at 65% by 2025 and 70% by 2030, while material recovery targets by 2031 require the recovery of 80% of lithium and 95% of cobalt, nickel and copper from spent batteries. In parallel, waste portable battery collection targets have been established at 51% by 2028 and 61% by 2031.

In parallel, the Critical Raw Materials Act (CRMA) [17] and the Net-Zero Industry Act (NZIA) [18], both adopted by the European Union in 2024, further reinforce the strategic importance of resource recovery, recycling, and domestic industrial capacity within the European framework. The CRMA was introduced to reduce the EU dependency on external suppliers of critical raw materials, particularly those required for renewable energy technologies, electric mobility, electronics, and energy storage systems. To strengthen supply chain resilience, the regulation establishes strategic targets for 2030, including at least 10% domestic extraction, 40% internal processing, and 25% of the annual EU consumption supplied through recycling. In parallel, the NZIA aims to accelerate the deployment and manufacturing capacity of net-zero technologies within Europe, promoting strategic sectors such as batteries, renewable energy systems, hydrogen technologies, carbon capture, and sustainable industrial processes. Within this framework, battery recycling is expected to play a crucial role in securing secondary sources of lithium, cobalt, nickel, manganese, graphite, and phosphorus-bearing compounds from end-of-life products. The rapid growth of electric vehicle deployment is anticipated to generate a substantial increase in spent lithium-ion batteries in the coming decades, making recycling technologies increasingly important not only for waste management but also for the development of a sustainable and strategically independent European raw materials supply chain.

1.3.1 Sewage Sludge Biomass

Sewage sludge (SS), a biomass by-product of municipal/industrial wastewater treatment plants (WWTPs), contains high concentrations of phosphorus (P), which has been extensively studied for potential recovery through additional biological and chemical processes integrated into various stages of wastewater treatment [19]. Initially, phosphorus in sludge was considered problematic due to its

contribution to eutrophication [20], necessitating its removal from both the water treatment stream and the sludge. However, with growing awareness of phosphorus's critical role in agriculture and concerns over its limited global availability [21] [22], the focus of research has shifted to P recovery. The purification process with P accumulation in the sludge will be explained in Section 2.2.1.

Over recent decades, the production of sewage sludge in Europe has significantly increased. Currently, around 8.1 million tons of wet sludge are produced annually in the EU, and ≈ 2 million tons from urban wastewater only in Italy [23], intensifying challenges related to its management. In both the Italian and broader European contexts, the generation and disposal of sewage sludge remain pressing issues with notable environmental and economic implications (48.000 tons of Italian urban SS are conferred abroad) [24]. Given the growing volume of waste, landfill disposal is no longer considered a sustainable option. Consequently, alternative treatment and reuse strategies, such as agricultural application, composting, and incineration, have gained prominence. European nations currently lack a unified approach to managing sewage sludge. According to Eurostat, several Southern and Eastern European countries, including Greece, Italy, Malta, Bosnia-Herzegovina, Romania, and Croatia, continue to rely on landfilling as the primary method of sewage sludge disposal. In contrast, nations such as The Netherlands, Germany, Slovenia, and Switzerland predominantly rely on incineration as their main treatment method [25]. Historically, the agricultural application of sewage sludge was widespread; however, this practice has increasingly been limited due to the presence of high levels of heavy metals (HM), pathogens, and toxic organic substances [26], prompting a shift toward alternative waste management strategies such as mono-incineration. Within this framework, it is recommended that only sludge meeting high-quality standards be applied directly to agricultural land. At the same time, the remainder should be directed to mono-incineration. The incineration of sewage sludge (SS) is considered a viable strategy for phosphorus (P) recovery. This approach not only enables energy production but also prevents the release of pollutants into the soil, as contaminants are either immobilized in ashes or dust or eliminated during the process. Moreover, sewage sludge ash (SSA), a combustion product of SS, exhibits a relatively high phosphorus content (4%–9%), comparable to that of low-grade phosphate rock [27] [28]. This offers a more sustainable alternative to conventional phosphate mining, avoiding many of its associated environmental and operational drawbacks. In Figure 6, the data about the amount of SS devoted to incineration according to the Eurostat; amounts are still limited but expected to rise in the next year. The picture does not account for the Italian scenario, where two incineration plants are found in Milan and Bologna, burning municipal SS landfilling the SSA, which to date has not found an effective reuse. Nevertheless, incineration alone does not eliminate the majority of heavy metals present in sewage sludge, and, depending on national regulations, this may pose challenges for the subsequent

use of sewage sludge ash (SSA) as a crop fertilizer [29]. Moreover, the P bioavailability in SSA is generally low, as most of the P is present in insoluble mineralized forms such as berlinite (AlPO_4), β -tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), and whitlockite ($\text{Ca}_{3-x}(\text{Mg}, \text{Fe})_x(\text{PO}_4)_2$), which are not suitable for direct use as fertilizers [30]. Consequently, improving the bioavailability of P, while carefully managing the presence of heavy metals, is a primary objective in P recovery from SSA. The most applied recovery methods include wet extraction and thermochemical processes [31].

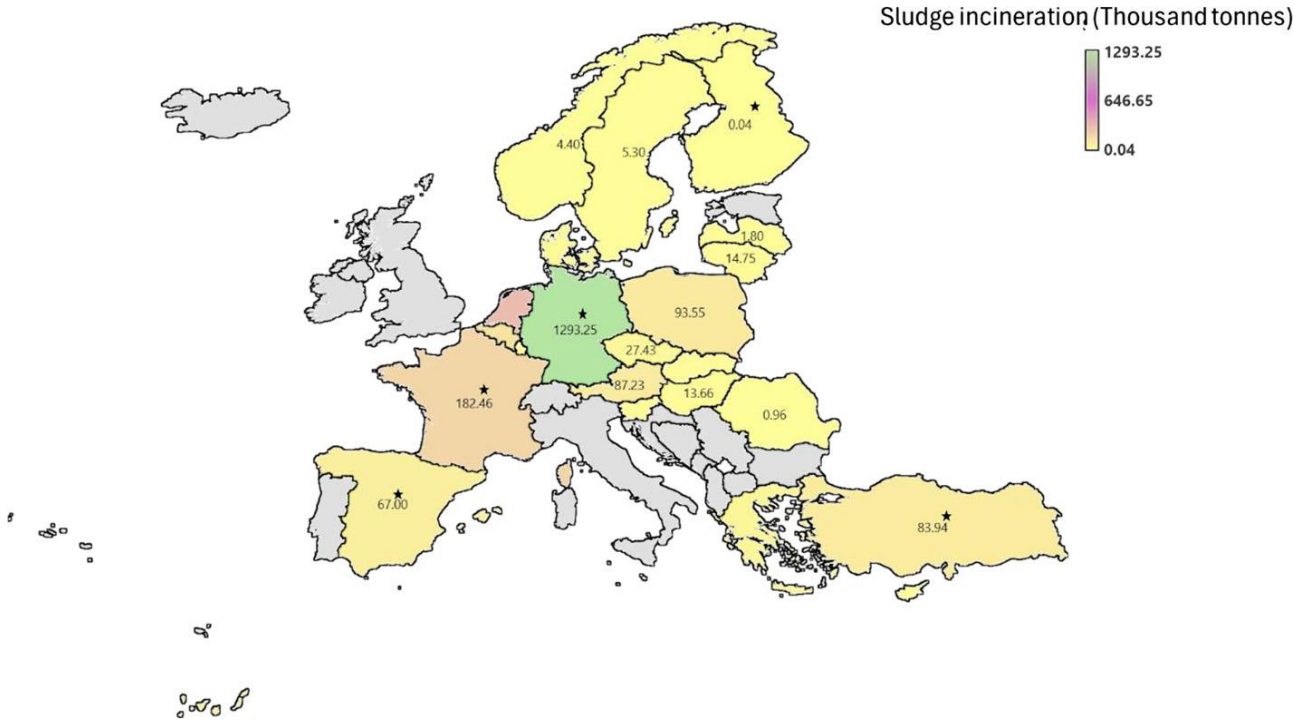


Figure 6: Annual quantity (in thousand tonnes) of urban sewage sludge destined for incineration. Data provided by the European Commission (2023) referring to the year 2021, except for Denmark, France, The Netherlands, Finland, and Turkey (2020); Germany (2019); and Spain (2018). No data are available for the regions shown in grey [32].

1.3.2 Lithium-Iron-Phosphate Batteries in the Lithium-Ion Battery (LIBs) Scenario

Lithium-ion batteries (LIBs) are composed of several key components: an anode (negative electrode), a cathode (positive electrode), a separator (a solid material that physically separates the anode and cathode), and an electrolyte (typically liquid) that facilitates the transport of lithium ions between the electrodes.

Depending on the chemical composition of the cathode, various LIB chemistries can be distinguished, including:

- **NCM**: lithium nickel cobalt manganese oxide ($\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$);

- **NCA**: lithium nickel cobalt aluminium oxide ($\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$);
- **LCO**: lithium cobalt oxide (LiCoO_2);
- **LMO**: lithium manganese oxide (LiMn_2O_4);
- **LFP**: lithium iron phosphate (LiFePO_4).

These chemistries exhibit distinct crystalline structures, which significantly influence battery performance: layered (LCO, NCA, and NCM), spinel (LMO), and olivine (LFP). The nature of the crystalline structure determines how lithium ions diffuse, which in turn affects the electrochemical properties of the battery [33] [34].

Layered cathode materials such as LCO (LiCoO_2), NCM (LiNiMnCoO_2), and NCA (LiNiCoAlO_2) are among the most commonly employed due to their high specific energy, making them suitable for high-power applications such as electric vehicles [35]. However, LCO-based cathodes suffer from limited cycle life and thermal/structural instability at high voltage, posing significant safety risks at elevated temperatures [36]. Furthermore, along with NCM and NCA, LCO chemistries rely heavily on critical raw materials, particularly cobalt and nickel, which are associated with supply chain constraints, environmental risks during disposal, and escalating costs due to complex extraction and limited recyclability [37]. LMO (LiMn_2O_4) cathodes, while less toxic and more affordable than their layered counterparts, exhibit lower thermal stability and reduced specific power output [38]. In contrast, olivine-structured materials such as LFP have emerged as highly promising alternatives. They offer exceptional thermal and chemical stability, intrinsic safety, and extended cycle life, primarily due to their robust crystal framework. Moreover, LFP utilises iron instead of critical metals like cobalt, nickel, or manganese, reducing both supply chain vulnerabilities and environmental impact. Additionally, the lower cost of iron contributes to a 30–40% reduction in overall battery production costs, depending on the size and energy rating of the battery pack. Despite the growing interest in LFP batteries, challenges remain. LFP batteries were first introduced in the 1990s and have emerged as one of the most promising types among lithium-ion batteries, even though they have not always been the preferred choice. Notably, their theoretical specific capacity is lower than that of NCA and NCM cathodes, pushing many LIB manufacturers toward high-voltage cathode chemistries to achieve greater energy density in smaller battery packs [38].

In LFP cells, as in other LIBs, the most common anode material is graphite; less frequently, graphene or lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) is used. Graphite is favoured primarily due to its high specific capacity, low average voltage, high conductivity, low cost, well-established manufacturing processes, and abundant availability.

The separator is a porous physical membrane impregnated with electrolytes, which serve as the standard medium for ionic conduction, enabling lithium ions to travel between the cathode and anode. Conventional liquid electrolytes in LFP batteries consist of approximately 83% by weight nonaqueous, carbonate organic solvents (either singly or in mixtures), 12% lithium salt (primarily lithium hexafluorophosphate, LiPF_6 , noted for its high toxicity and reactivity with air and water), and 5% organic additives dissolved in the solvent.

On the cathode side, active material is coated onto an aluminium foil, often with polyvinylidene fluoride (PVDF) used as a binder, to attach the active material to the aluminium substrate. The active material itself is a powder composed of lithium iron phosphate, LiFePO_4 (LFP).

From a chemical perspective, the battery operates through the transfer of lithium ions between the cathode and anode via the separator and electrolyte, driven by the potential difference between the two electrodes. However, the interfacial electrolyte is unstable, leading to a series of reactions that form interfacial layers between the electrolyte and both the anode and cathode. In particular, a thin film, predominantly composed of lithium fluoride (LiF) resulting from the decomposition of LiPF_6 , typically forms on the anode surface. This film is electronically insulating yet chemically permeable. During charging, the cathode releases lithium ions that intercalate into the anode, while during discharging the reverse process occurs, with lithium ions moving back to the cathode and releasing energy. In effect, each charge–discharge cycle involves the reversible transition of the crystal from a lithium-rich phase, LiFePO_4 , to a lithium-depleted phase, FePO_4 .

The distinct properties of LFP batteries are largely attributed to the unique olivine crystal structure of LiFePO_4 , in which lithium (in LiO_6 octahedra) and iron (in FeO_6 octahedra) occupy octahedral sites and the phosphate group (PO_4) resides in tetrahedral sites [39] [40] (Figure 7).

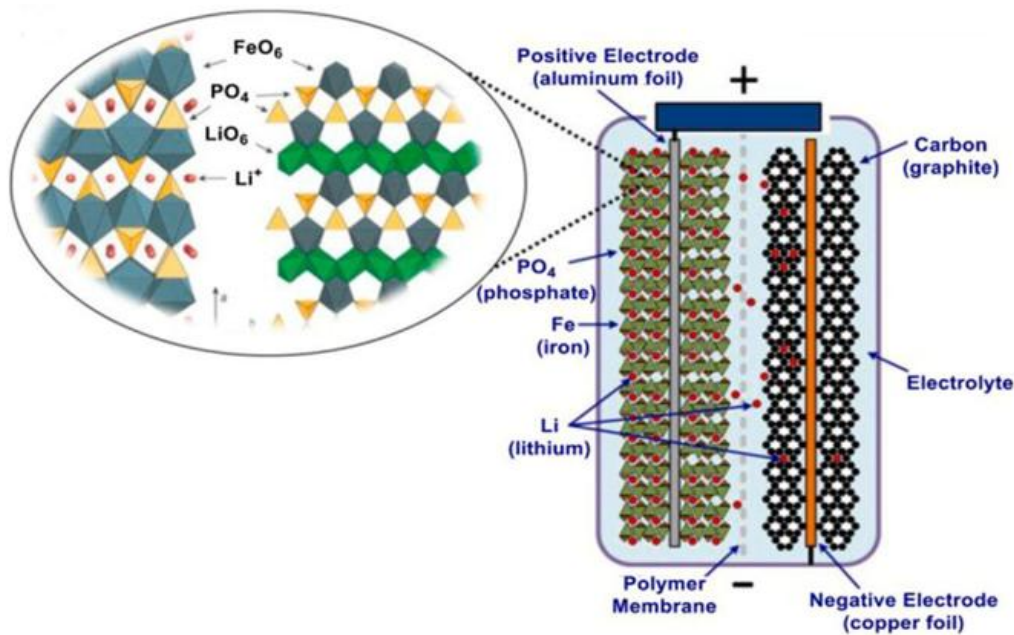


Figure 7. LFP structure; anode (LiFePO_4) and cathode (C) [40].

This particular structure confers several advantages [41]:

- **Economic Viability:** LFP batteries use readily available and inexpensive materials, making them less costly than traditional batteries, up to 30% lower production costs.
- **Thermal Stability:** The presence of phosphate (PO_4) groups affords significant thermal resistance, with the material remaining stable up to $700\text{ }^\circ\text{C}$, which is advantageous for applications experiencing high thermal stress.
- **Extended Cycle Life:** LFP cells exhibit superior longevity; while other lithium-ion batteries typically offer up to 1,500–2,000 charge cycles, LFP batteries can exceed 2,000 cycles. This durability is partly due to the relatively low mechanical stress imposed on the cathode during operation [41].
- **Enhanced Safety:** LFP batteries are considered the safest among lithium-ion types due to their reduced flammability and higher heat tolerance. Thermal runaway—a phenomenon leading to battery fires—is less likely to occur with LFP cells, whose temperature threshold for thermal runaway is around $270\text{ }^\circ\text{C}$ compared to $210\text{ }^\circ\text{C}$ for NMC and $150\text{ }^\circ\text{C}$ for NCA. Moreover, the stronger Fe–PO bond in LFP compositions (compared to the Co–O bond in cobalt-based batteries) makes it more difficult to dislodge oxygen atoms under chemical or physical stress (e.g., short-circuiting or overheating) [41]. Consequently, LFP batteries are more likely to withstand rapid temperature increases without sustaining permanent damage or, in extreme cases, igniting [41].

- *Fast Energy Delivery:* They have lower internal resistance, which facilitates rapid energy discharge.
- *Complete Discharge Without Severe Damage:* Their design allows for complete discharge without incurring significant deterioration.
- *Low Maintenance Costs:* Combined with the aforementioned factors, the overall cost of ownership for LFP batteries is lower, despite their lower energy density relative to other battery types.

On the other hand, some disadvantages must be considered:

- *Lower Energy Density:* LFP batteries have a lower energy density compared to NMC batteries. This implies that, to achieve equivalent range, an LFP pack must either be larger and heavier or, at equal size and weight (as in electric vehicles), result in a reduced driving range. However, the gap in energy density is narrowing—from a previously cited 70% difference to approximately 20–25% today.
- *Lower Voltage:* With a nominal voltage of 3.2 V (compared to 4.2 V for other lithium-ion chemistries), LFP batteries generally experience slower charging. Nonetheless, the development of next-generation products is starting to achieve charge rates comparable to other lithium-ion batteries [41].
- *Poor Intrinsic Electronic Conductivity:* LFP's intrinsic electronic conductivity is very low. Researchers, including the French scientist Michel Armand, have demonstrated that incorporating carbon nanotubes and reducing particle size can mitigate this limitation [39].

What makes lithium iron phosphate (LFP) batteries particularly compelling is that, at the end of their service life, they represent an excellent source of secondary raw materials [42]. Their composition makes them well-suited for various recovery and treatment processes. In particular, the spent batteries contain significant amounts of lithium (Li) and phosphorus (P), with phosphorus present in concentrations that are consistently relevant, typically ranging from approximately 15% to 50% by weight, depending on the specific pre-treatment [43].

LFP batteries are expected to become increasingly widespread in the coming years (Figure 8) due to their superior thermal stability, lower production costs, and the absence of critical metals such as cobalt and nickel. These features, combined with their long cycle life and excellent chemical stability, make LFP cells particularly suitable for stationary energy storage and mid-range electric vehicles, leading to their growing adoption compared to other lithium-ion chemistries.

1.4 Overview of Treatment Processes for SSA and LFP and Their Role in Phosphorus Recovery

The main treatment approaches for sewage sludge ash (SSA) and lithium iron phosphate (LFP) are typically categorized into two broad types: wet processes and thermal processes. Wet processes involve the use of acid leaching to solubilize the solid-phase components by converting them into ionic forms. This is followed by selective precipitation steps aimed at recovering specific target compounds of interest, such as phosphorus or metals. These methods are particularly advantageous for achieving high selectivity and purity, although they often require careful control of pH and the management of secondary waste streams.

Thermal processes, in contrast, rely on high-temperature reactions to induce structural and chemical transformations within the materials. These reactions can be carried out with or without the addition of external reagents, depending on the specific treatment objective. As such, thermal methods offer a promising route for the valorisation of waste materials by enhancing their functionality and reducing their environmental impact.

1.4.1 Wet Treatments

Wet chemical extraction is a widely used and relatively simple method that involves contacting a solid sample with a solvent (extractant) to promote the dissolution of nutrients and soluble salts. This technique can be easily applied at the laboratory scale and scaled up to pilot plant applications by adjusting various parameters, such as contact time, liquid-to-solid (L/S) ratio, temperature, extractant concentration, and mixing conditions. In both cases (SSA and LFP), the extractant is usually an inorganic/organic acid (H_2SO_4 , H_3PO_4 , HCl , HNO_3 , and $\text{C}_6\text{H}_8\text{O}_7$), in different concentrations [30] [44] [45].

1.4.2 Wet Extraction of Sewage Sludge Ashes

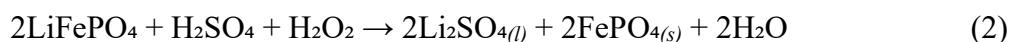
In the SSA case scenario, several of the above-mentioned acids can be used to improve P leachability of the ash. It is a challenging process, involving the leachability of not only major elements such as sulfur (S), calcium (Ca), phosphorus (P), potassium (K), magnesium (Mg), iron (Fe), aluminium (Al) and silicon (Si) but also certain amounts of heavy metals (HMs) such as zinc (Zn), copper (Cu), lead (Pb), and nickel (Ni). [46]. An example is the one reported by Boniardi et al. [47] using 0.2 M of H_2SO_4 with a liquid-to-solid ratio (L/S) of 20 (i.e. 1g of SSA and 20 mL of acid) for a contact time of 2 hours in stirring conditions. This procedure ensures an efficient P dissolution with minimal co-dissolution of hazardous and toxic elements (HMs). After leaching, the solid part is separated from the leachate through filtration. The leachate undergoes a titration process using 1% lime solution to

raise the pH to 9 and promote phosphate precipitation. Even when the co-dissolution of toxic elements is not entirely avoided, the concentration of heavy metals in the recovered product (the precipitate) generally remains within acceptable limits for use in agricultural applications. In some instances, minor exceedances may occur for elements (arsenic, copper, or zinc). The presence of elevated levels of toxic elements is a critical factor affecting the quality and safety of the final product and may necessitate additional purification steps. Nonetheless, the recovered material typically exhibits a high phosphorus content and favourable bioavailability, making it a promising candidate for use as a secondary phosphorus source [47].

The principle behind wet extraction from SSA is quite similar to the traditional industrial method used for phosphorus recovery from PRs. However, while the latter has been optimized and refined over decades of industrial application, the recovery of phosphorus from SSA remains in its early stages of research and development. Continuous efforts are still needed to obtain a purified and usable phosphorus product. This field of research is still emerging and requires testing of a wide range of SSA types and treatment procedures to identify the most effective solutions. The SSA is chemically and mineralogically more complex than PR and often varies significantly depending on its origin and the SS combustion system. Therefore, material characterisation is considered a crucial initial step in developing efficient and tailored recovery strategies.

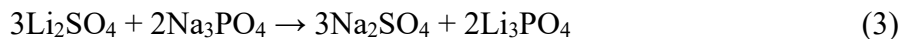
1.4.3 Wet Extraction of Lithium-Iron-Phosphate Spent Batteries (Black Mass)

The treatment of spent LFP batteries typically starts with discharge and dismantling, followed by shredding and physical separation processes. Additional treatments, including pyrolysis and fine milling, are subsequently applied to obtain a powder fraction commonly known as LFP black mass (BM). The BM is treated with different organic/inorganic acids to dissolve and recover different compounds. The wet extraction applied to LIBs is a hydrometallurgical reaction. An example is reported by Huan Li et al. [45] using a stoichiometric amount of H_2SO_4 (0.3 M) and hydrogen peroxide (H_2O_2) at 60 °C with a retention time of 2 hours to selectively dissolve Li from the LiFePO_4 structure, collecting Fe and P in the solid residue. The process occurs according to the following reaction (2):



H_2SO_4 provides H^+ ions to enhance lithium leachability, and H_2O_2 oxidizes Fe^{2+} to Fe^{3+} , promoting rodolicoite (FePO_4) formation and precipitation, while lithium bonds with SO_4^{2-} , ends up in the solution in Li_2SO_4 form. The FePO_4 solid residue is then treated at 600 °C for 4 hours to get rid of

the carbon slag, coming from the coating of the cathode, and purify the material. The addition of sodium phosphate dodecahydrate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$), in the stirred solution at 65 °C containing Li_2SO_4 , favours the precipitation of Li_3PO_4 according to reaction (3):



The mixture is then filtered, and the precipitate is washed with 80 °C deionized water to eliminate the excess of Na_3PO_4 .

Phosphorus is recovered in the form of FePO_4 , losing approximately 2 % of the total amount during the H_2SO_4 leaching, while the Li, precipitated in the form of $\text{Li}_3\text{PO}_4 \approx$ the 96 % of the total amount. Others proposed methods involve the usage of organic acids like citric acid, succinic acid, and acetic acid [48] [49] with a thermal pre-treatment to activate the powder and eliminate the carbon. The treatment is always carried out with the employment of H_2O_2 as an oxidizing agent. P and Fe are always recovered in the form of FePO_4 , and Li in the carbonated form zabuyelite (Li_2CO_3), thanks to the addition of Na_2CO_3 in the Li enriched solution.

The main problem of these techniques, even if they allow an optimal recovery, is the excessive number of steps: filtrations, evaporations, and thermal treatments at medium-high temperatures. Also, a high number of chemical agents are used, which have a high cost in the process. For example, organic acids are inevitably more expensive than those of conventional mineral acids. Given that the recycling of spent LiFePO_4 batteries is generally less economically attractive compared to the recycling of other lithium-ion batteries (LIBs) containing high-value metals such as cobalt and nickel, maintaining cost-effectiveness is a significant challenge, and using inorganic ones as H_2SO_4 , can lead to a less expensive process [45] .

1.5 Thermochemical Treatments

Thermochemical treatment involves the intimate mixing of biomass-derived ash or the black mass powder with selected chemical additives, most commonly carbonates and sulfates [50] [51] [52] [53] [54,55] [55] or chloride-based compounds [56] [57] [58] [59], followed by thermal processing at elevated temperatures ranging from 500 to 1500 °C [60]. This procedure facilitates the transformation of phosphorus species within the sample from poorly soluble/plant-unavailable forms to more bioavailable or soluble phases. The vision is to form more easily leachable compounds or compounds that can be individually recovered after treatment for use in the industrial supply chain. Concurrently, the thermal regime promotes the volatilization of heavy metals (HMs), thereby decreasing their concentration in the final product. As a result, the treated ash can be repurposed as a phosphorus-rich

fertilizer with significant potential for application as a raw material in sustainable agriculture [61] [62].

Despite its promising outcomes, the primary limitation of this approach lies in its high energy requirements, particularly when implemented using conventional furnace technologies. Nevertheless, optimizing key process parameters—such as energy input, additive selection and dosage, and target phosphorus bioavailability—can yield a favourable balance that enhances both the economic feasibility and agronomic value of the resulting product [63].

1.5.1 Sewage Sludge Ash Thermochemical Treatments

Thermochemical methods represent a pivotal class of high-temperature technologies that facilitate the extraction and purification of phosphorus (P) from sewage sludge ash (SSA) through mineral phase transformation. Among these, the AshDec and Mephrec processes are frequently cited as prominent examples. The AshDec process exhibits high efficacy in the recovery of volatile heavy metals; however, its efficiency markedly diminishes for non-volatile heavy metal species. In contrast, the Mephrec process employs a shaft furnace configuration for phosphorus recovery, although it is associated with substantial energy demands and limitations concerning soil acidity remediation [64] [65]

A relatively streamlined alternative is found in the Thermphos process, which utilizes SSA as a feedstock in an electric arc furnace operating at approximately 1500 °C. In this configuration, phosphorus is recovered in the form of elemental tetraphosphorus (P_4), with coke serving as reductant. During this process, gaseous P_4 , carbon monoxide (CO), and volatilized metals are collected and subsequently condensed, whereas non-volatile constituents, including calcium and silicon, are retained in the form of a reusable slag phase [66] [67].

Of particular interest is the thermochemical treatment of incineration ash—a method favoured for its operational simplicity and minimal infrastructure requirements. Such treatments have been shown to significantly enhance the bioavailability of phosphorus, a phenomenon attributed to the formation of novel mineral phases such as chlorapatite ($Ca_5(PO_4)_3Cl$), farringtonite ($Mg_3(PO_4)_2$), and stanfieldite ($Ca_4Mg_5(PO_4)_6$). Notably, treatment with magnesium chloride ($MgCl_2$) at 1000 °C has resulted in phosphorus solubility as high as 97% in citric acid—a proxy for plant-available P [61] [68] demonstrated that co-incineration of sewage sludge with 10% calcium, in the form of $CaCl_2$, led to a marked improvement in phosphorus solubility, reaching up to 60% in a 2% citric acid solution. However, comparative studies revealed that magnesium chlorides yielded not only a higher phosphorus recovery rate but also improved plant uptake efficiency relative to calcium-based additives. This approach underpins the Ecophos technology, which employs a reducing thermal

environment (pyrolysis) followed by leaching with phosphoric acid (H_3PO_4) to extract phosphorus from the residual ash, ultimately producing a merchant-grade H_3PO_4 product.

In contrast, the SPODOFOS process utilizes aluminothermic reduction to convert phosphate compounds within the ash into elemental phosphorus at approximately $600\text{ }^\circ\text{C}$, capturing the volatilized phosphorus for subsequent recovery [69]. Both methods are particularly suited to sewage sludge ash (SSA) streams characterised by high volumes and elevated heavy metal content, where traditional land application poses environmental and regulatory concerns.

1.5.2 Lithium-Iron-Phosphate Black Mass Thermochemical Treatments

Thermochemical approaches have also been applied to the regeneration of lithium iron phosphate (LFP) batteries. One such method involves heating a mixture of spent LFP, citric acid (CA), and eutectic lithium salts ($\text{LiNO}_3\text{:LiOH}$ in a 3:2 molar ratio) at temperatures ranging from 350 to $550\text{ }^\circ\text{C}$ for four hours. Following thermal treatment, the resulting powder is washed with deionized water to remove excess lithium salts. The regenerated LFP is then centrifuged and dried at $80\text{ }^\circ\text{C}$ for 12 hours. This eutectic Li^+ -assisted roasting strategy offers a relatively simple and energy-efficient route for cathode material recovery, creating favourable conditions for regeneration while enabling straightforward product recovery and minimizing energy consumption [70].

A related salt-assisted roasting process is characterised by a multi-step protocol:

- Pre-treatment of end-of-life batteries, including disassembly and preparation of the cathode materials;
- Mixing the recovered cathode powder with sodium carbonate (Na_2CO_3) and graphite, where sodium carbonate serves as a fluxing agent, promoting the breakdown of Fe-PO_4 bonds in the LiFePO_4 crystal structure, and graphite acts as a reducing agent, aiding in the reduction of iron and other oxidized metals;
- Thermal treatment in a tubular furnace under an inert nitrogen atmosphere. The roasting conditions—temperature and duration—are optimized to maximize the conversion efficiency. During this process, LiFePO_4 is transformed into iron oxides and water-soluble lithium compounds;
- Leaching of the roasted material using water or other suitable solvents, allowing lithium to dissolve into solution while iron oxides remain as solid residues. The lithium is then precipitated as lithium phosphate (Li_3PO_4).

This integrated approach enables the recovery of both lithium and iron, and also offers the potential for reusing the leaching solution in subsequent processing cycles, thereby supporting a circular economy model.

One of the key advantages of this method lies in its energy efficiency and its reduced reliance on hazardous chemicals, making it a more sustainable option for battery recycling. However, successful implementation requires precise control of operational parameters and initial investment in specialized equipment for salt-assisted carbothermic roasting, which may pose practical challenges. Nonetheless, the method presents considerable potential for the eco-efficient and economically viable recovery of critical materials from spent LFP cathodes [71].

1.6 Research Objectives and Scope of the Thesis

The main objective of this thesis is to investigate and control the phase transformations of phosphorus-bearing materials derived from secondary inorganic resources, with the aim of enhancing phosphorus recovery through a fundamental understanding of their mineralogical evolution.

In contrast to conventional approaches primarily focused on maximising extraction yields, this work adopts a materials-oriented perspective, where the redistribution of phosphorus among crystalline phases is considered, the key factor governing its reactivity and leachability. Attention is therefore devoted to identifying, quantifying, and understanding the formation of new phases generated during thermochemical treatments.

In this framework, the thesis focuses on two highly relevant yet still underexplored secondary materials: sewage sludge ash (SSA), derived from the mono-incineration of wastewater treatment sludge, and black mass obtained from spent lithium iron phosphate (LFP) batteries following dismantling and mechanical processing. These materials, although significantly different in origin and composition, share a common challenge related to the presence of phosphorus in stable and poorly soluble crystalline phases.

The characterisation is carried out through an integrated analytical approach combining chemical analysis, X-ray powder diffraction with quantitative phase analysis (XRPD-QPA), and Scanning Electron Microscopy coupled with energy dispersive spectroscopy (SEM-EDS), with the objective of elucidating phase composition, elemental distribution, and microstructural features of these complex materials.

Building on this detailed characterisation, the thesis further investigates non-conventional treatment strategies aimed at modifying the crystalline structure of the materials, with particular emphasis on phosphorus-bearing phases, and enhancing phosphorus recovery. Two main approaches are explored. The first approach focuses on SSA and involves CO₂ mineralisation processes followed by acid leaching, with the aim of promoting phosphorus mobilization through carbonation-induced pH reduction.

The second approach investigates microwave-assisted thermochemical treatments applied on SSA and LFP black mass in the presence of alkaline reagents at different temperatures, coupled with subsequent leaching in low environmental impact solutions. These thermochemical treatments are specifically designed to induce controlled phase transformations and promote the formation of new crystalline products.

Within this framework, phosphorus recovery is not limited to its extraction in solution but also considers its redistribution and potential stabilization within newly formed solid phases, for the potential direct reuse of these materials, depending on their physicochemical properties.

Through the combination of advanced characterisation techniques and tailored thermochemical processes, this work aims to establish a direct relationship between phase evolution, structural modifications, and phosphorus solubilization behaviour in complex inorganic matrices.

To address these objectives, the thesis is structured into three main chapters.

- Chapter 2 focuses on the carbonation of SSA, providing insights into wastewater treatment residues and investigating the behaviour of SSA during and after CO₂ mineralisation and the subsequent acid leaching.
- Chapter 3 presents a more comprehensive characterisation of SSA and of the products obtained after microwave thermochemical treatment, with particular emphasis on phase evolution and rigorous experimental analysis.
- Chapter 4 is dedicated to LFP batteries, addressing both the characterisation of the black mass and the investigation of its microwave thermochemical treatment, with particular emphasis on the scientific relevance of the newly formed phases, which may open new perspectives for high-tech applications, including advanced cathode materials, solid electrolytes, and functional phosphate-based systems.

2. Exploring the Potential of Sewage Sludge Ash for CO₂ Sequestration and Resource (P) Recovery

As discussed in Chapter 1, phosphorus in natural phosphate rocks is predominantly hosted within mineral phases such as apatite and its variants, which are typically processed through acid-based routes to enable phosphorus extraction. The effectiveness of these processes is strongly governed by the mineralogical composition of the material, including the presence of calcium phosphates and associated silicate phases.

A similar mineralogical framework can be observed in sewage sludge ash (SSA), where phosphorus is commonly incorporated into calcium-, iron-, and aluminium-based phosphate phases. This compositional analogy suggests that SSA can be considered, to some extent, as a secondary phosphate resource, although with a higher degree of heterogeneity and structural complexity compared to natural phosphate rocks.

However, despite these similarities, the direct application of conventional acid leaching strategies to SSA is often limited by the stability of its crystalline phases and by the presence of competing elements.

This chapter therefore investigates the behaviour of SSA under carbonation conditions, with the aim enhance phosphorus mobility with sulfuric acid.

Abstract

Sewage sludge incineration produces sewage sludge ash (SSA), a by-product that has garnered growing interest due to its potential for phosphorus (P) recovery. Among its prospective applications, the use of SSA as a fertilizer is particularly promising. However, its direct application in agriculture is hindered by the low bioavailability of nutrients. Additionally, SSA exhibits potential for carbon dioxide (CO₂) sequestration via carbonation, attributed to its calcium-rich composition. This carbonation process may also enhance phosphorus extraction by reducing the buffering capacity of the system, thereby leading to lower pH values during leaching.

This study presents the first application of a fluid-phase (slurry) high-pressure carbonation process to SSA, aiming to promote mineralisation and carbonate formation. The most effective results were obtained from an SSA sample with the higher calcite content (~28%), achieving CO₂ sequestration of approximately 20 kg per metric ton of dry SSA. Despite this, carbonation did not significantly enhance phosphorus leachability under acid extraction conditions compared to untreated SSA.

Notably, this work reveals, for the first time, a strong correlation between the amorphous phase content of SSA and its phosphorus leaching efficiency. Extraction efficiency ranged from 0.7% for a

sample with 15.2% amorphous content to 52.1% for a sample with 42% amorphous content. These findings highlight the potential of combining carbonation with additional treatment strategies to optimize SSA for both agricultural use and CO₂ capture, laying the groundwork for future research.

Keywords: Carbonation, Mineralisation, P-recovery, Circular economy

Scientific contribution

The samples analysed in this chapter were collected thanks to the collaboration with MM S.p.a. in the RHIGUS project (LOW ENERGY TECHNOLOGIES FOR RECOVERY OF HIGH-GRADE PHOSPHORUS) financed by MUR: PRIN 2022. This work was also supported under the scope of the Next-GenerationEU (Italian PNRR – M4 C2, invest 1.3 – D.D. 1551.11-10-2022, PE000000004) within the MICS (Made in Italy–Circular and Sustainable) Extended Partnership.

The content presented in this chapter is the result of my original work, encompassing the literature review, data curation, formal analysis, investigation, methodology development, conceptualization, and writing. Contributions made by other researchers are duly acknowledged and attributed to the original authors within the text. Additionally, certain results included in this chapter are derived from the following publication. The content has been adapted in form and structure to ensure consistency with the format and requirements of this doctoral thesis.

- Massa, M., Calce, S., Pachaiappan, P., Valentim, B., Punta, C., D'Anna, A., ... & Bontempi, E. (2025). Exploring the potential of sewage sludge ash for CO₂ sequestration and resource recovery. *Journal of Water Process Engineering*, 71, 107153.

2.1 Introduction

Sewage sludge incineration is a widely implemented practice in several European countries, including The Netherlands, Switzerland, Austria, and Germany [52]. This thermal treatment serves the dual purpose of eliminating organic contaminants and generating heat. As a by-product of this process, sewage sludge ash (SSA) is produced, which retains concentrated levels of certain heavy metals and, notably, phosphorus (P), typically ranging from 4% to 12%. This concentration is comparable to that found in low-grade phosphate rock (2%–18% P) [72].

SSA consists of a complex mixture of crystalline phases, the formation of which is largely governed by the temperature and duration of incineration [73]. These phases commonly include quartz (SiO₂), hematite (Fe₂O₃), berlinite (AlPO₄), anorthite (Ca(Al₂Si₂O₈)), amorphous or poorly crystalline hydroxyapatite (Ca₅(PO₄)₃OH), and a variety of phosphate minerals such as rodolicoite (FePO₄), farringtonite Mg₃(PO₄)₂, and whitlockite (Ca_{3-x}(Mg, Fe)_x(PO₄)₂) [74] [75] [76,77] [77]. Among these,

whitlockite is identified as the predominant phosphorus-bearing mineral phase in SSA, frequently associated with or encapsulated in hematite [75]. In addition to its crystalline components, SSA often contains varying amounts of amorphous phases, as confirmed by detailed mineralogical characterisations [78].

Phosphorus in SSA is primarily present in low-solubility mineral forms, necessitating acid leaching to mobilize the more soluble phosphate fractions [47]. Alternatively, thermochemical treatment of SSA with sodium-based additives has been shown to transform calcium phosphate phases such as $\text{Ca}_3(\text{PO}_4)_2$ into more plant-available forms like buchwaldite (NaCaPO_4). This process yields mineral phases with enhanced agronomic value due to their increased bioavailability [55] [79] [80].

Phosphorus (P) extraction from sewage sludge ash (SSA) remains limited due to its predominantly low-solubility mineral phases. Nonetheless, the potential for SSA recycling exists in the field of construction materials, particularly due to its chemical composition, which closely resembles that of cement [81]. As such, SSA has been investigated for use as a binder, a partial replacement for cement, an additive in mortar formulations, and as a substitute for fine aggregates [82]. The presence of amorphous phases in SSA has been shown to enhance pozzolanic reactions during the later stages of concrete curing, potentially improving mechanical performance [82].

In particular, SSA rich in calcium oxide (CaO) has demonstrated promise when used as a partial replacement for fine aggregates, contributing to increased concrete density and, consequently, enhanced compressive strength [83]. However, other studies have reported that SSA exhibits lower pozzolanic activity compared to more conventional supplementary cementitious materials such as coal fly ash. These differences are primarily attributed to compositional variations [84].

The variability in SSA composition and its consequent applications reported in the literature can be largely attributed to the differing incineration conditions under which sewage sludge is treated. Key operational parameters—such as combustion temperature, residence time, and the type of fluidizing medium used—significantly influence the final characteristics of the ash. For instance, increasing the incineration temperature beyond 800 °C for short residence times can lead to the volatilization and reduction of certain heavy metals such as Zn, Cd, and Pb, while Ni and Cr remain relatively unaffected [85]. In contrast, longer residence times (up to 3 hours) have been associated with increased ceramic content (e.g., aluminosilicates) and a reduction in soluble salts such as Na^+ , K^+ , and Mg^{2+} [18]. Furthermore, pre-stabilization with lime during sludge processing has been reported to produce SSA with altered mineralogical compositions and significantly enhanced reactivity compared to conventionally produced ash [82] [86].

Beyond construction applications, SSA may also offer value in environmental remediation, particularly through carbon dioxide (CO_2) sequestration via mineral carbonation. This process, which

utilizes industrial alkaline waste materials rich in CaO and MgO, enables the long-term storage of CO₂ in the form of stable carbonate minerals. During carbonation, CO₂ reacts with these alkaline oxides in the presence of water, forming calcium or magnesium carbonates and effectively immobilizing the greenhouse gas in a solid and durable form [87].

Two main carbonation approaches are recognized: direct carbonation, where CO₂ is applied directly to the waste material—often under controlled humidity or aqueous conditions—and indirect carbonation, which involves extracting reactive components from the waste prior to CO₂ exposure. The efficiency of both processes is highly dependent on various factors, including particle size, surface area, porosity, and moisture content. Finer particles with greater surface areas facilitate more effective CO₂ diffusion and reaction. Likewise, adequate moisture promotes CO₂ dissolution and the subsequent formation of carbonate ions, accelerating the mineralisation process. Higher CO₂ concentrations and pressures enhance solubility, while optimal temperatures (typically moderate) are required to maintain favourable reaction kinetics and avoid competing reactions that may inhibit carbonate formation. Pre-treatment techniques such as grinding or thermal activation can further enhance reactivity by exposing fresh reactive surfaces. However, impurities and heavy metals present in the waste may interfere with carbonation kinetics or affect the stability of the resulting carbonates [88].

Carbonation has been extensively studied for various industrial waste materials [89], and over the last decade, significant progress has been made in the development of CO₂ mineralisation and utilization (CMU) technologies for alkaline solid wastes [88] [90] including applications involving carbonated rocks in deep geological storage [89]. Nevertheless, to date, there have been no published studies specifically investigating the potential of SSA for CO₂ sequestration.

This study presents, for the first time, an evaluation of SSA sourced from an industrial facility in Northern Italy as a potential material for CO₂ mineralisation. The goal is to assess its carbonation capacity and explore its viability as a secondary resource for CO₂ capture at or near emission sources [91]. This approach responds to the urgent global need to mitigate climate change by developing scalable methods to reduce atmospheric CO₂ through mineralisation. In addition, the effect of carbonation on phosphorus extraction efficiency is also investigated, offering a dual-purpose strategy that aligns with both environmental and resource recovery goals.

2.2 Experimental

2.2.1 Materials

Three SSA samples were collected from a wastewater treatment facility near Milan (Italy), which operates a waste-to-energy plant for the incineration of municipal sewage sludge (SS). The sludge is combusted at 850 °C in a fluidized bed reactor using silica sand as the bed material, with an estimated residence time of 2–3 minutes. To mitigate acid gas emissions, CaCO_3 is added during the process. The overall wastewater purification and sludge treatment workflow ahead of the incineration is illustrated in Figure 8. Phosphorus removal from the wastewater is achieved through a combination of biological and chemical treatments. The biological pathway relies on phosphorus-accumulating organisms (PAOs), whereas the chemical pathway involves dosing ferric chloride (FeCl_3), which promotes P-precipitation. The precipitated phosphorus, primarily in the form of FePO_4 , is subsequently removed via filtration. Samples SS1 and SS2 were obtained under conditions of high FeCl_3 dosage coupled with limited biological removal, whereas SS3 was produced with lower FeCl_3 input and enhanced biological removal. The FeCl_3 dosage also influences the resulting ash color: SSA_1 and SSA_2 exhibit a darker red/brown appearance, while SSA_3 is lighter in color due to the greater contribution of PAOs in phosphorus removal and the presence of CaCO_3 for flue gas treatment.

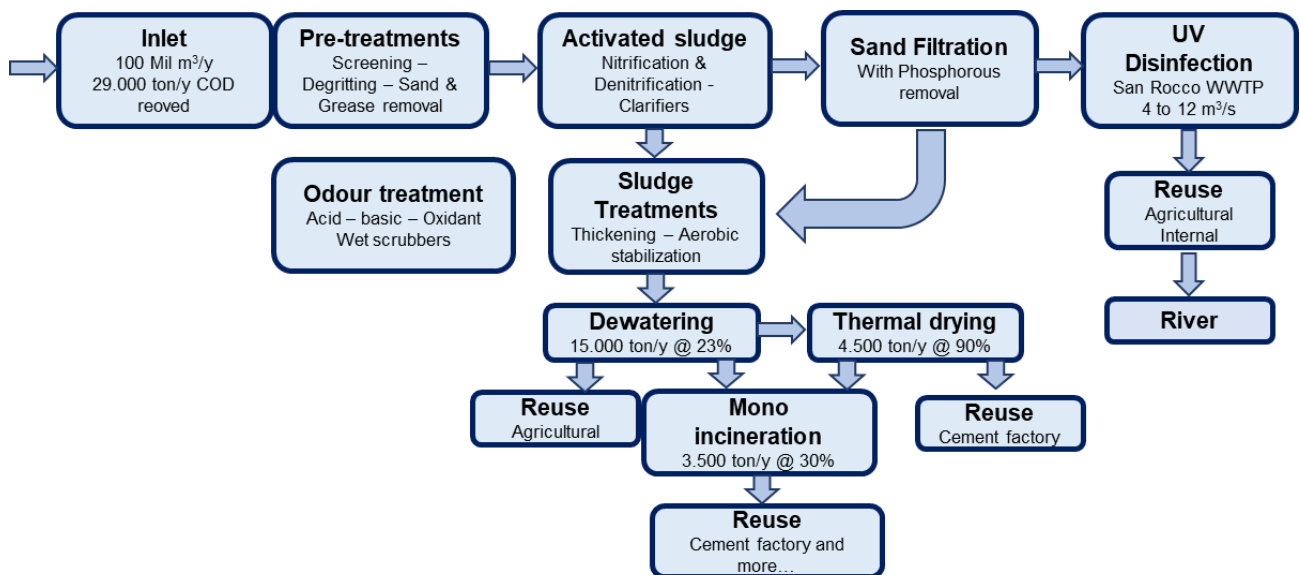


Figure 8. The process flow diagram of the wastewater treatment plant outlines two parallel lines: water treatment and sludge treatment. The water treatment line starts with wastewater collection, followed by preliminary operations such as screening, grit removal, and oil separation. It then proceeds to biological treatment for the removal of organic matter, coupled with nitrification and denitrification processes. Clarifiers are employed for sludge sedimentation. Phosphorus removal follows, after which the water undergoes sand filtration and final disinfection by UV irradiation. The sludge treatment line begins with the sludge withdrawn

from the clarifiers, which is subjected to thickening and aerobic stabilization to reduce water content and organic load. This is followed by dewatering and thermal drying stages. The resulting dried and/or dewatered sludge is subsequently directed either for reuse or for mono-incineration

Before incineration, the sewage sludge underwent thickening to reduce water content and volume, followed by aerobic stabilization to decrease organic matter, inhibit the proliferation of pathogenic microorganisms, and improve overall manageability. Subsequent steps included dewatering at 100 °C and/or thermal drying at 270 °C. Dewatered sludge is black (Figure 9A), with a sharp and acrid odour, and displays a shovelable - muddy consistency, with a dry matter content of 21–25%. Thermally dried sludge is also black (Figure 9B) but has a harsher, acrid odour and a dry, powdery texture, with 89–90% of dry matter. A combined mixture of dewatered and thermally dried sludge presents intermediate physical properties, containing 32–33% of dry matter. The combustion of this mixed sludge reduced the methane demand for sustaining incineration, requiring approximately 45.5 Sm³/ton.

The 3 SSA samples, obtained with different processes, are the following:

- SSA_1: derives from SS1 (dewatered)
- SSA_2: derives from SS2 (thermally dried)
- SSA_3: derives from SS3 (dewatered), burned in the combustion chamber after a bed material replacement to enhance temperature control, a higher dosage of CaCO₃ to control the acid emissions, and a major employment of PAOs for P biological removal.

The calcium carbonate dosage required to obtain SSA_3 was approximately 70–80 kg per ton of dry matter fed. Given that the sludge contained 21–22% of dry matter, this corresponded to about 16 kilograms of CaCO₃ per ton of sludge. Sludge combustion was performed in the facility illustrated in Figure 10, operated at 850 °C with a residence time of 2 seconds, in compliance with current legislation [92].

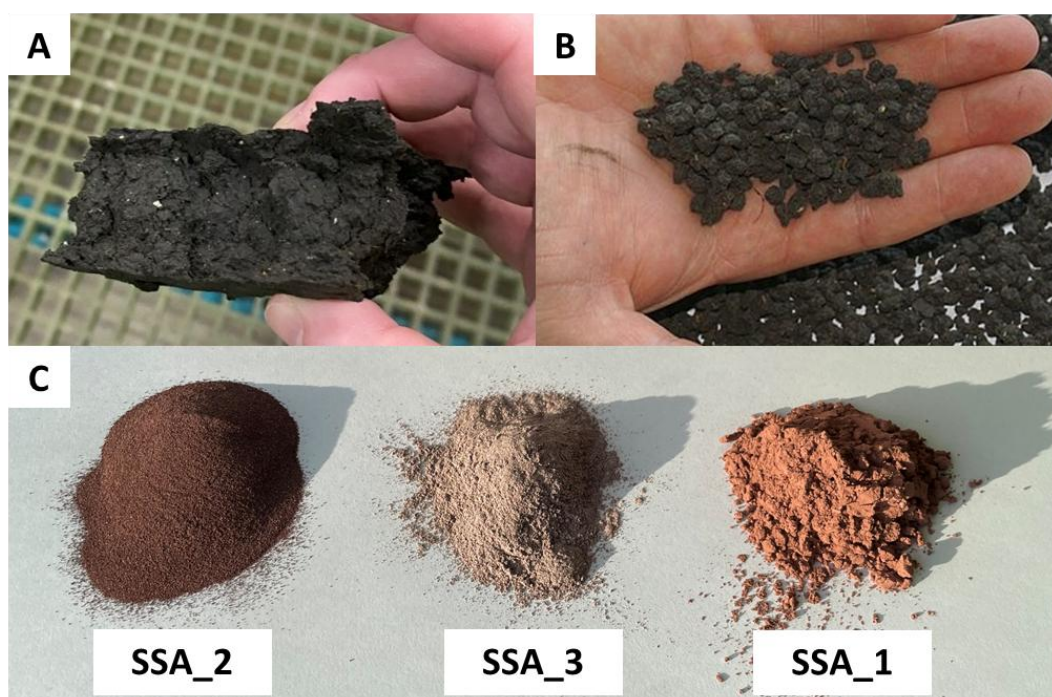


Figure 9. A) dewatered SS; B) thermally dried SS; C) resulting SSAs after the combustion.

The temperature was monitored near the internal wall of the combustion chamber (Figure 10). Under these conditions, the sludge was effectively converted into an inert material, namely SSA.

Dehydrated and/or dried sewage sludge was stored in two separate silos within the experimental area and fed independently into the furnace. From the hopper, dehydrated sludge was pumped into the combustion chamber, while calcium carbonate was stored in a dedicated hopper and pneumatically injected. Dried sludge was pneumatically conveyed to an injection lance in the thermo-oxidative reactor, where thermal oxidation reactions took place. The resulting gas streams were directed to the energy recovery section. First, the heat was transferred to cold air via a heat exchanger to maintain self-sustaining combustion conditions, and then to an air–water cooling circuit. The heated water was subsequently circulated to a cooling tower for dissipation and recirculation.

Following energy recovery, flue gases are passed through a treatment system combining dry (bag filters) and wet (scrubber) processes to ensure compliance with emission standards. Purified gases were then released through the stack, where continuous monitoring guaranteed regulatory conformity. Ashes originating from both combustion and flue gas treatment were collected in big bags at the ash unloading station. Typically, the amount of SSA produced corresponded to about 10% of the mass of incinerated sewage sludge.

Ash characterisation was performed using ICP-OES to quantify total phosphorus and X-ray diffraction with an internal standard to determine crystalline phases and amorphous content. Additionally, SEM-EDS imaging was employed to examine the condition of calcite crystals.

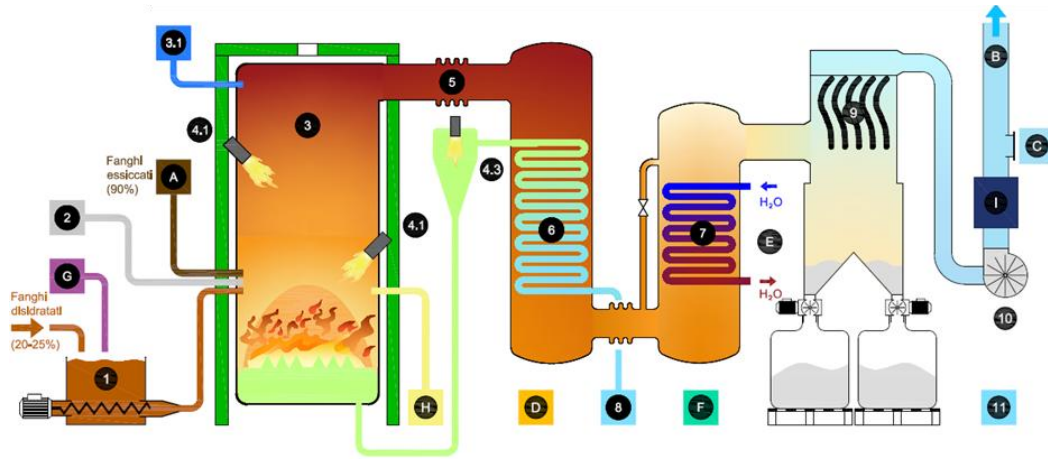


Figure 10. Plant diagram: 1) Sludge injection; 2) Big-bag and limescale dosage; 3) Combustion oven; 3.1) Temperature regulator; 4.1) Burners; 4.3) Preheating burner; 5) Duct; 6) Air/air exchanger for energy recovery; 7) Energy recovery air/water exchanger; 8) Fluidization air compressor; 9) Dry filter; 10) Centrifugal fan, 11) Air compressor; B) Chimney.

2.2.2 Acid Digestion and Wet Extraction with Sulfuric Acid

Acid digestion was carried out on 1 g of SSA sample using 100 mL of aqua regia (HNO_3 : HCl = 1:3, v/v) at 70 °C for 5 h to ensure complete dissolution of the powder and allow the determination of total phosphorus concentrations. Wet extraction was performed following the procedure reported by Boniardi et al. [47]. Briefly, 1 g of ash was mixed with 20 mL of 0.2 M H_2SO_4 (liquid-to-solid ratio of 20) and stirred at room temperature for 2 h. The resulting suspension was then filtered through a 0.45 μm nylon membrane. The reagents used included nitric acid (HNO_3 , CAS no. 7697-37-2, purity >65%) and sulfuric acid (H_2SO_4 , CAS no. 7664-93-9, purity 95–97%) purchased from Carlo Erba, and hydrochloric acid (HCl , CAS no. 7647-01-0, purity 37%) supplied by Sigma-Aldrich.

2.2.3 Carbonation Trial

Carbonation experiments were performed in a Berghof Reactor Heating System (BR-300) at ambient temperature (25 °C). Each test was carried out on a slurry prepared with 30 g of SSA and 45 mL of Milli-Q water (L/S = 1.5), magnetically stirred at 30 rpm for 24 h. The resulting material was subsequently dried at 105 °C in an oven.

CO_2 sequestration was quantified assuming ideal gas behaviour [93], according to (4):

$$n = P_{\text{drop}} V/RT \quad (4)$$

where P_{drop} is the pressure drop, V is the volume of the reactor tank occupied by water (0.355 L), T is the reactor temperature (≈ 25 °C), and R is the gas constant ($0.08314472 \text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). A blank test with the same volume of pure water was performed to evaluate CO_2 adsorption by water [26]. This contribution was subtracted from the total pressure drop to determine the amount of CO_2 consumed by the carbonation reaction.

2.2.4 Characterisation Techniques

2.2.4.1 X-ray Powder Diffraction (XRPD) and Quantitative Phase Analyses (QPA)

X-ray diffraction (XRD) analyses were performed using an X'Pert Pro diffractometer (PANalytical, Malvern, UK) equipped with an X'Celerator detector and Cu anode ($\text{CuK}\alpha$, $\lambda = 1.5406 \text{ \AA}$), operating at 40 kV and 40 mA. Samples were prepared using the up-loading technique, and diffraction patterns were collected over the $10\text{--}75^\circ$ 2θ range. Quantitative phase analysis (QPA) was carried out by Rietveld refinement (Profex 5.2.2) using alumina ($\approx 10 \text{ wt\%}$, Carlo Erba, CAS no. 1344-28-1) as an internal standard.

2.2.4.2 Scanning Electron Microscopy and Energy Dispersive X-ray Spectrometry (SEM-EDS)

Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) was performed at the Materials Centre of the University of Porto (CEMUP, Portugal) to investigate carbonate crystal formation. Samples were mounted on carbon tape and sputter-coated with a thin carbon film to improve conductivity. Analyses were conducted using an FEI Quanta 400 FEG ESEM/EDAX Genesis X4M, operated in high-vacuum mode at 15 kV with a beam spot size of 4.5. Secondary electron (SE) imaging was used for surface topography, while the backscattered electron (BSE) mode was employed for phase identification. Semi-quantitative elemental analysis of selected regions was carried out via EDS microanalysis.

2.2.4.3 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and pH

Phosphorus content was quantified by ICP-OES (PerkinElmer Optima 8300 SD) at wavelengths 213.617, 214.914, and 178.221 nm, with a detection limit of 0.05 mg/L. All measurements were performed in triplicate. A Fluka 51474 TraceCERT standard ($1002 \pm 4 \text{ mg/L}$ stock solution) was used and diluted as required for calibration.

The pH of the solutions/slurries was measured with a Metrohm 827 Lab pH-meter (Origgio, Italy). For leaching in Milli-Q water, tests were performed according to the Italian Fertilizer Scientific Center protocol using a liquid-to-solid ratio of 16.66 (3 g in 50 mL) and a mixing time of 30 min. Additional pH measurements were conducted following leaching in 0.2 M H₂SO₄.

2.3 Results and Discussion

2.3.1 Characterisation of the as-collected Samples of Sewage Sludge Ashes

ICP-OES chemical analyses revealed that the overall phosphorus content exhibited only moderate variations among the three investigated samples. Specifically, SSA_1 contained 7.79 ± 0.2 wt% P, SSA_2 contained 8.27 ± 0.2 wt% P, and SSA_3 contained 6.19 ± 0.2 wt% P, resulting in a maximum difference of approximately 2 wt%. Although these differences are relatively small, they provide useful indications of the intrinsic variability in the chemical composition of the materials under investigation.

The results obtained from the XRD characterisation of the as-received SSA samples are presented in Table 1, while an example of the diffraction pattern is reported in Figure 11. The crystalline phases containing phosphorus were found to be diverse, with whitlockite identified as the principal P-bearing phase, present in amounts ranging from 7.5 to 11.1 wt%. In addition to whitlockite, hydroxyapatite was consistently detected. Tetra-potassium pyrophosphate was observed exclusively in SSA_1 and SSA_2, and monetite was detected only in SSA_3. The occurrence of these phases highlights differences in both the mineralogical composition and the thermochemical transformation pathways of phosphorus during the incineration process. Beyond the phosphorus-containing phases, the SSA samples also displayed several other crystalline constituents of significant relevance (Table 1). Quartz was systematically observed and can be attributed to the silica sand employed as bed material during combustion. Calcite was detected with particular abundance in SSA_3, reflecting the higher dosage of carbonate materials that had been introduced in this case to mitigate the emission of acid gases. Furthermore, lime was identified as a product of carbonate decomposition, whereas portlandite was formed by the hydration of lime [94], owing to its natural tendency to absorb atmospheric moisture. These phase transformations and interactions can be summarized through the chemical reactions (5 & 6) reported in the literature [94] [95], which describe the sequential decomposition and hydration pathways of carbonate-derived compounds as follows:



This sequence of reactions accounts for the highest Ca(OH)_2 content observed in the SSA_3 sample (12.6 wt%). In addition, significant amounts of hematite (Fe_2O_3), associated with phosphorus removal through FeCl_3 addition, and anhydrite (CaSO_4) were consistently detected in all three SSA samples.

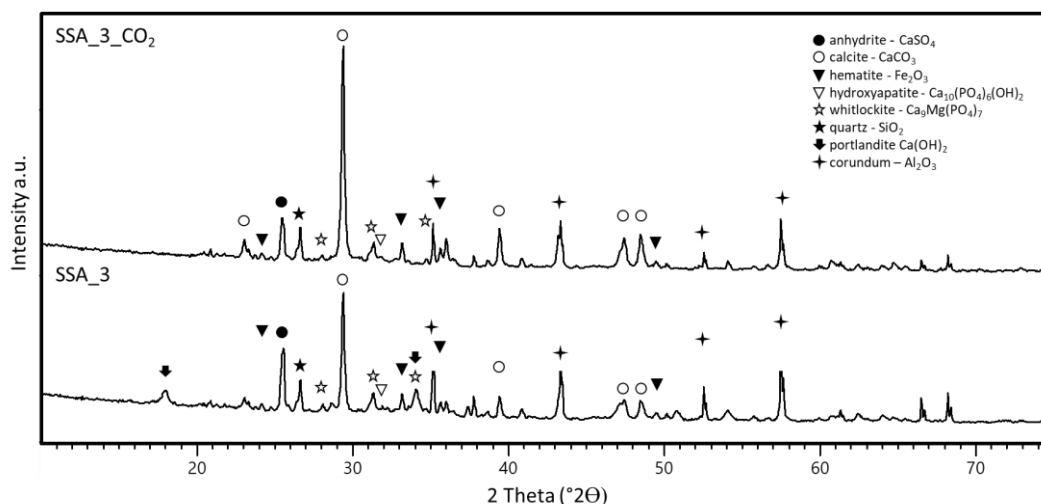


Figure 11. X-ray Diffraction Pattern of SSA_3 (bottom) and SSA_3 after the high-pressure CO_2 absorption (top).

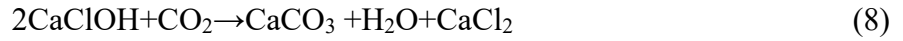
The mineralogical differences among the samples can be explained by the fact that each underwent distinct combustion pathways, which were the result of the varying experimental conditions applied in the pilot furnace. These controlled variations were specifically designed to explore and define the most favourable operational parameters for the production of SSAs.

Table 1. Quantitative Phase Analysis of the as-collected SSA; R_{wp} is the refinement agreement factor; χ^2 is the goodness-of-fit statistic from the Rietveld refinement.

Crystalline phases		SSA_1	SSA_2	SSA_3
name	chemical formula			
anhydrite	$CaSO_4$	4.8 (2)	7.0 (4)	9.0 (4)
calcium hydroxychloride	$CaClOH$	0.9 (1)	0.4 (1)	0.5 (1)
lime	CaO	0.6 (1)	1.7 (2)	1.4 (1)
calcite	$CaCO_3$	7.7 (4)	10.6 (3)	28.2 (9)
portlandite	$Ca(OH)_2$	-	-	12.6 (5)
goethite	$FeO(OH)$	1.3 (2)	1.1 (1)	0.5 (1)
hematite	Fe_2O_3	9.7 (5)	9.3 (3)	4.4 (2)
hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	3.6 (3)	5.4 (3)	4.7 (2)
K ₄ - pyrophosphate	$K_4P_2O_7$	1.6 (2)	2.1 (1)	-
whitlockite	$Ca_9Mg(PO_4)_7$	11.0 (4)	11.1 (4)	7.5 (3)
quartz	SiO_2	11.7 (2)	12.3 (3)	3.9 (1)
sulfur	S_8	1.3 (1)	2.0 (3)	1.6 (1)
tridymite	SiO_2	2.1 (1)	1.5 (1)	3.8 (2)
albite	$NaAlSi_3O_8$	0.9 (1)	-	-
magnesium sulfate	$MgSO_4$	0.2 (1)	0.9 (1)	1.0 (1)
srebrodolskite	$Ca_2Fe_2O_5$	0.6 (1)	1.5 (1)	1.9 (1)
monetite	$CaHPO_4$	-	-	3.1 (3)
magnesite	$MgCO_3$	-	-	0.7 (1)
amorph		42.00 (14)	33.1 (9)	15.2 (7)
Crystalline phosphorus	P	3.21	3.65	3.05
R_{wp}		2.11	2.60	3.12
χ^2		2.89	2.45	3.01

2.3.2 High-Pressure CO₂ Absorption Results

Figure 12 presents the results of the carbonation tests performed on the SSA_2 sample, expressed in terms of CO₂ pressure drop. The carbonation process of SSA in aqueous media proceeds through several consecutive stages. Initially, CO₂ dissolves from the gas phase into the aqueous solution. The dissolved CO₂ then migrates towards the liquid–solid interface, followed by its diffusion through the solid passivation layer that progressively forms on the particle surface. Ultimately, at the active solid interface, the carbonation reaction can effectively take place according to the following chemical pathways (7 & 8) [29,30]:



The formation of calcium carbonate during carbonation leads to the development of a passivation layer, which progressively limits the transport of CO_2 to the reaction interface. Depending on the reaction conditions, different deposition mechanisms of the carbonation products can occur, influencing both the structure of the passivation layer and the rate of CO_2 diffusion as the reaction progresses.

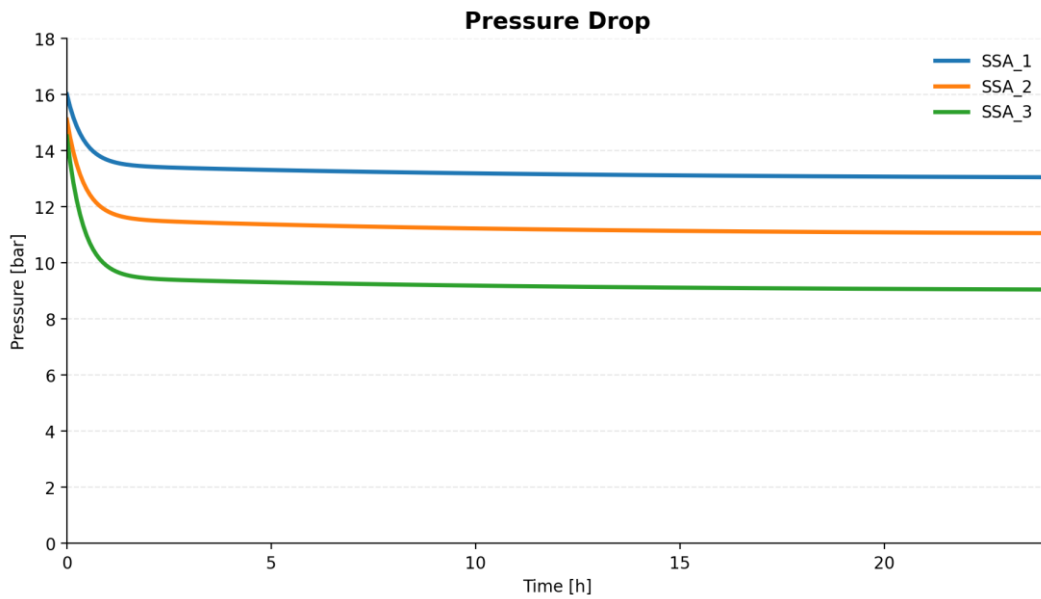


Figure 12. pressure drop for SSA_1 (red) SSA_2 (blue) and SSA_3 (green).

The behaviour of the pressure (P) curve (Figure 12) as a function of time is initially linear, up to approximately 30–40 minutes. This stage corresponds to the rate-controlling step of CO_2 absorption, which is governed by the diffusion of CO_2 through the liquid film adjacent to the gas–liquid interface [96]. As the reaction proceeds, the dissolved CO_2 migrates to the liquid–solid interface and subsequently diffuses through the passivation layer. At this stage, the carbonation reaction takes place at the active solid interface, leading to calcium carbonate precipitation [96].

In the later stages of the process, the controlling mechanism is primarily the diffusion of CO_2 through the passivation layer. Under these conditions, the carbonation reaction follows first-order kinetics and occurs exclusively at the active sites of the ash surface. The evolution of the process can also be monitored by recording the reactor temperature (Figure 13), which rises due to the exothermic nature of carbonation. The reaction gradually slows down and appears to reach completion after approximately 14 hours, when the temperature stabilizes back to baseline.

Table 2 reports the amount of CO₂ absorbed by the SSA samples, calculated using the gas law in combination with Rietveld refinement and quantitative phase analysis (QPA). The QPA results are further detailed in Table 3. For the SSA_3 sample, the sequestration capacity was estimated at approximately 20 kg of CO₂ per ton of dry matter.

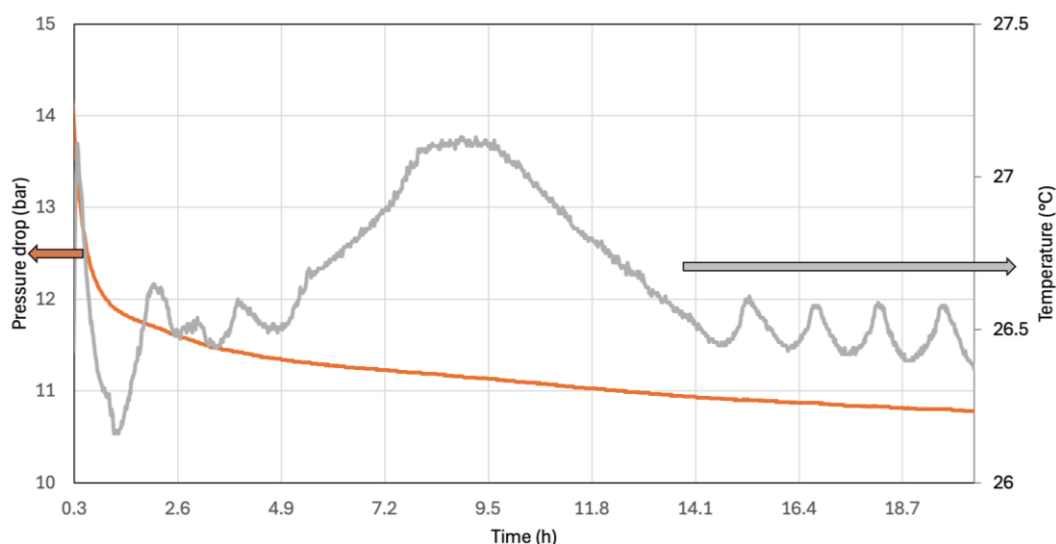


Figure 13. Pressure drop and reactor temperature recorded during the carbonation experiment of the SSA_2 sample. The pressure drop exhibits a linear trend in the early stage, corresponding to the initial diffusion of CO₂ into the system. The temperature profile highlights the progression of the carbonation reaction.

Table 2. Real pressure drop and the evaluated CO₂ amount absorbed (abs.) by gas law and QPA analysis.

Sample	ΔP (bar)	ΔP (bar) drop (without P water drop)	CO ₂ mass (g) abs. by gas law	CO ₂ mass (g) abs. by QPA
SSA_1	4.74	1.84	1.16	0.91
SSA_2	4.50	1.60	1.01	0.60
SSA_3	6.68	3.78	2.38	2.27

2.3.3 Quantitative Phase Analysis after CO₂ absorption

Following forced carbonation, the CaCO₃ content increased in all samples (Table 3), corresponding to a net CO₂ absorption capacity of 3.03 wt%, 2.02 wt%, and 7.56 wt% for SSA_1, SSA_2, and SSA_3, respectively (according to the QPA analysis). Nevertheless, the carbonation pathways differed among the samples as a consequence of their distinct mineralogical compositions, as revealed by XRD analyses.

In SSA_1, the CaCO₃ content increased by approximately 6.9 wt%, which can be attributed to the complete carbonation of Ca(OH)₂ and calcium chloride hydroxide (CaClOH) crystalline phases. In this case, however, a reduction in the amorphous phase content was also observed, most likely due to the crystallisation of amorphous Ca-containing phases into calcite (Table 3).

For SSA_2 and SSA_3, the increase in calcite content after forced carbonation was approximately 4.6 wt% and 17.2 wt%, respectively. This trend can be directly correlated with the higher amounts of Ca(OH)₂ present in the as-received samples, further emphasizing that SSA_3 exhibits the greatest potential for CO₂ capture. In addition, other noteworthy transformations in SSA_3 involved the partial hydration of CaSO₄ into bassanite and gypsum, as well as the hydration of monetite into brushite (CaHPO₄·2(H₂O)). In these cases, the amorphous content increases, which is expected if the calcite doesn't crystallize properly, maintaining an amorphous structure.

Table 3. Quantitative Phase Analysis of the as-collected SSA; R_{wp} is the refinement agreement factor; χ^2 is the goodness-of-fit statistic from the Rietveld refinement.

Crystalline phases		SSA_1	SSA_2	SSA_3
name	chemical formula	CO ₂	CO ₂	CO ₂
anhydrite	$CaSO_4$	6.1 (3)	5.4	6.4 (2)
bassanite	$CaSO_4 \cdot 0.5(H_2O)$	-	-	0.5 (1)
gypsum	$CaSO_4 \cdot 2H_2O$	-	-	0.4 (1)
calcite	$CaCO_3$	14.6 (4)	15.2 (5)	45.4 (9)
goethite	$FeO(OH)$	0.6 (1)	1.2 (1)	0.6 (1)
hematite	Fe_2O_3	8.3 (3)	7.9 (3)	3.9 (2)
hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	3.3 (2)	3.6 (2)	3.0 (2)
K ₄ - pyrophosphate	$K_4P_2O_7$	1.5 (1)	2.5 (2)	-
whitlockite	$Ca_9Mg(PO_4)_7$	10.6 (4)	9.8 (3)	6.5 (3)
quartz	SiO_2	10.8 (3)	11.6 (3)	4.6 (2)
sulfur	S_8	1.0 (1)	3.2 (3)	1.6 (2)
tridymite	SiO_2	2.2 (2)	2.0 (1)	1.2 (1)
albite	$NaAlSi_3O_8$	2.3 (2)	-	-
magnesium sulfate	$MgSO_4$	0.4 (1)	0.7 (1)	0.4 (1)
srebrodolskite	$Ca_2Fe_2O_5$	0.3 (1)	1.1 (1)	1.0 (1)
monetite	$CaHPO_4$	-	-	2.9 (2)
magnesite	$MgCO_3$	-	-	0.5 (1)
brushite	$CaHPO_4 \cdot 2(H_2O)$	-	-	0.4 (1)
amorph		38.0 (14)	35.8 (17)	20.7 (8)
Cr. phosphorus	P	3.04	3.11	2.60
R_{wp}		2.38	2.69	2.67
χ^2		2.85	2.97	2.91

2.3.4 Scanning Electron Microscopy Observations

SEM-EDS analyses were performed on both the as-collected and carbonated samples to investigate the formation of secondary carbonates and to highlight the differences in the morphology and crystallographic features of $CaCO_3$ particles. As illustrated in Figure 14A, the surface topography of the as-collected samples revealed $CaCO_3$ particles with partially decomposed structures, as evidenced by fragmentation, fissures, cracks, and the loss of well-defined crystal edges and faces. These features are indicative of the thermal stress and structural degradation experienced by the crystalline phases during combustion within the waste-to-energy plant chamber. In contrast, the samples subjected to forced carbonation displayed a partial restoration of the crystallographic structure of calcite (Figure 14B). In these samples, the particle surfaces were covered with newly formed calcite crystals, which

were nanometric in size (<40 nm) in SSA_2 (Figure 14C). These nanocrystals were not abundant enough to be detected by XRD. In SSA_3, however, the newly formed calcite crystals were micrometric in size (1–4 μm) (Figure 14D) and exhibited a well-defined morphology, with clearly visible CaCO_3 layering planes characteristic of accretion and deposition processes occurring in fluid systems.

The differences observed in the morphology of newly formed CaCO_3 crystals are most likely related to the experimental conditions, particularly the relative CO_2 pressure, which was initially set at 15 bar and gradually decreased during the 24-hour reaction period. Throughout this process, accretion and deposition of CaCO_3 appeared to take place on the surface of the pre-existing, partially decomposed crystals, thereby promoting their structural restoration and the development of more ordered morphologies. In other cases, the decomposed CaCO_3 crystals acted as nucleation sites for newly formed nanocrystals. For instance, Figures 14E and 14F depict a partially decomposed CaCO_3 sand bed grain (approximately 80 μm) entirely covered with a dense layer of newly formed calcite nanocrystals.

Overall, the SEM-EDS observations corroborate the XRD results. The predominance of nanocrystalline CaCO_3 with sub-crystalline structures in SSA_2 supports the hypothesis of amorphous calcite formation. This interpretation is consistent with the discrepancy observed between the CO_2 uptake values obtained from gas law calculations and those derived from Rietveld refinement, and also with the amount of amorphous phase detected pre- and post-carbonation. Notably, SSA_2 exhibited the largest deviation between the two methods, further validating the presence of amorphous calcite in this sample.

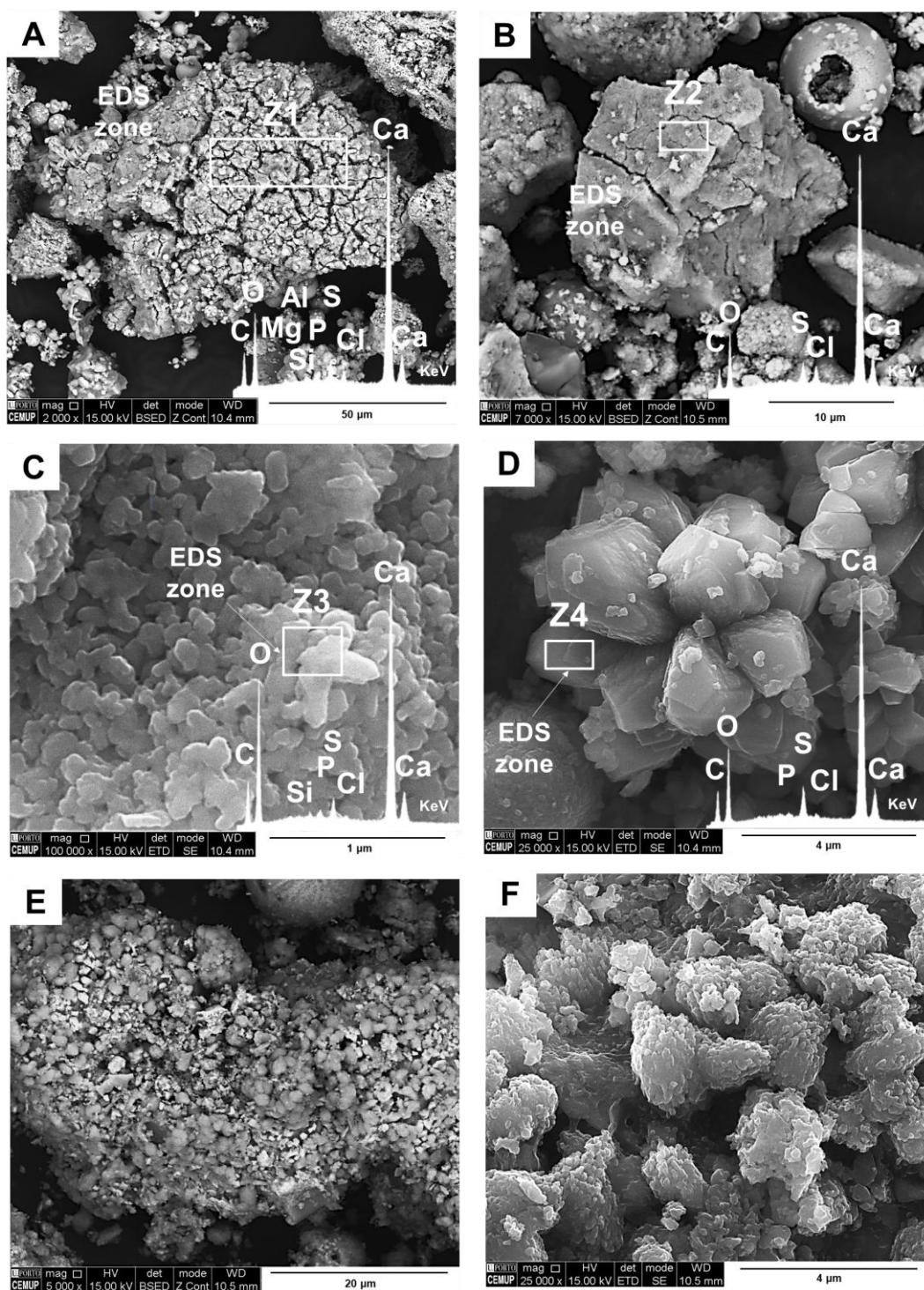


Figure 14. SEM-EDS analyses of CaCO_3 particles before and after forced carbonation trials: (A) partially decomposed CaCO_3 sand bed grain with corresponding EDS spectrum of zone Z1 (sample SSA_1; BSE mode; 2000 $\times$); (B) restored calcite crystal with EDS spectrum of zone Z2 (sample SSA_3; BSE mode; 7000 $\times$); (C) newly formed calcite nanocrystals with EDS spectrum of zone Z3 (sample SSA_2; SE mode; 100000 $\times$); (D) newly formed calcite crystals after forced carbonation (sample SSA_1; SE mode; 25000 $\times$); (E) surface of a partially decomposed CaCO_3 sand bed grain covered by newly formed calcite crystals (sample SSA_1; BSE mode; 5000 $\times$); (F) magnified view of panel E showing newly formed calcite crystals (sample SSA_1; SE mode; 25000 $\times$).

2.3.5 Influence of Carbonation on P-extraction with H₂SO₄ on Sewage Sludge Ashes

As shown in Table 4, carbonation led to a significant decrease in the slurries' pH for samples SSA_1 and SSA_2, from 12.6 to 7.5 and 7.7, respectively, whereas SSA_3 exhibited a smaller reduction, from 12.5 to 9.0. According to the literature [97], phosphorus extraction is strongly dependent on the final pH of the leaching solution, a relationship confirmed by the ICP-OES data reported in Table 4. To evaluate whether a lower starting pH could enhance phosphorus recovery under the same acid dosage, P-extraction tests were conducted using 0.2 M sulfuric acid with a 1:20 solid-to-liquid (S/L) ratio. The final pH values obtained (Table 4) indicate that for SSA_1 and SSA_2, as well as their carbonated counterparts (SSA_1_CO₂ and SSA_2_CO₂), phosphorus extraction was essentially unaffected by carbonation. For instance, SSA_1 showed P-extraction values of 40,606.4 ± 1000.7 mg/kg and 38,201.9 ± 1000.1 mg/kg for the as-received and carbonated samples, respectively. After recalculation of the carbonated sample values to account for CO₂ dilution, the extraction efficiencies were nearly identical: approximately 51–52 % for SSA_1/SSA_1_CO₂ and 37–39 % for SSA_2/SSA_2_CO₂ (Table 4).

Table 4. Total amount of P in the samples as collected; Total amount of P recalculated according to the CO₂ uptake dilution factor; pH of the solutions of the samples as collected, after carbonation, and after H₂SO₄ 0.2 M leaching test; P extracted using H₂SO₄ and P extraction efficiency.

Sample	P tot mg/kg			pH	pH H ₂ SO ₄ treated	P extraction mg/kg			Extraction efficiency %
SSA_1	77873	±	1561	12.6	1.6	40606	±	1000	52.1
SSA_1 CO ₂	74974	±	1503	7.5	1.6	38201	±	1000	51.0
SSA_2	82719	±	1559	12.6	1.6	30910	±	999	37.4
SSA_2 CO ₂	80025	±	1508	7.7	1.6	31189	±	999	39.0
SSA_3	61892	±	1558	12.5	7.7	442	±	20	0.7
SSA_3 CO ₂	57449	±	1446	9.0	5.0	1829	±	40	3.2

In contrast, SSA_3 exhibited different behaviour. The final leachate pH values for SSA_3 and SSA_3_CO₂ were 7.7 and 5.0, respectively. Despite this significant reduction in pH, phosphorus extraction increased only marginally, reaching 1829.5 ± 40.0 mg/kg (3.2 % of total P) for SSA_3_CO₂. This outcome is consistent with previous findings [97], which demonstrate that P extraction remains low above pH 5.0 in such materials.

The limited effect can be attributed to the high CaCO_3 content in SSA_3. During acid leaching, CaCO_3 reacts with H_2SO_4 , generating CO_2 , water, and secondary salts such as calcium chloride, calcium oxalate, and gypsum [98]. These reactions consume free hydrogen ions (H^+), thereby reducing the availability of acid to dissolve phosphorus-bearing phases [99] [100] [101]. Consequently, phosphorus extraction efficiency is reduced.

Moreover, the lower amorphous content of SSA_3 compared with SSA_1 and SSA_2 further constrained P recovery. Since phosphorus is more readily leached from amorphous phases than from crystalline ones, the dominance of crystalline phases in SSA_3 contributed to its particularly low extraction yield. Therefore, despite its relatively high CaCO_3 content, SSA_3 showed only minimal improvement in P extraction following carbonation, underscoring the limitations of this approach for enhancing phosphorus recovery.

2.3.6 X-ray data and Quantitative Phase Analysis of the Solid Residue After Using 0.2 Molar of Sulfuric Acid (H_2SO_4)

Through X-ray and QPA analysis, it was possible to quantify the amount of crystalline phosphorus incorporated into phosphate structures, which amounted to 3.21 wt%, 3.65 wt%, and 3.05 wt% for SSA_1, SSA_2, and SSA_3, respectively. These values indicate that a substantial portion of phosphorus is hosted in the amorphous phase, corresponding to 42.0 wt%, 33.0 wt%, and 15.2 wt% for SSA_1, SSA_2, and SSA_3, respectively. In terms of phosphorus content, this corresponds to values ranging from 3.14 wt% (SSA_3) to 4.62 wt% (SSA_2). Figure 15, which compares the total phosphorus content determined by chemical analysis with the crystalline phosphorus fraction estimated by Rietveld refinement, clearly shows that phosphorus in the amorphous fraction is higher than in crystalline phases, in agreement with previous findings [75].

Table 5 summarizes the mineralogical results for the solid residues obtained after acid leaching with 0.2 M H₂SO₄, and Figure 16 represents the diffraction patterns of SSA_3 after the leaching test and after the CO₂ absorption and leaching test. For both untreated and carbonated samples (SSA_1_leached, SSA_2_leached, SSA_1_CO₂_leached, and SSA_2_CO₂_leached), complete dissolution of phosphorus-containing crystalline phases was observed, as whitlockite, hydroxyapatite, and tetrapotassium pyrophosphate were not detected. In contrast, in SSA_3, the acid dosage proved insufficient to achieve complete dissolution of the crystalline phases, as whitlockite was still detected at concentrations of approximately 4.5 wt% and 2.5 wt% for the untreated and carbonated samples, respectively. However, other P-bearing crystalline phases, such as monetite and hydroxyapatite, were not detected and are therefore assumed to have been completely dissolved.

Certain phases, such as Fe₂O₃ and SiO₂, were not affected by the acid treatment, reflecting their persistence from the pre-leaching composition. Regarding the amorphous fraction, SSA_3 and SSA_3_CO₂ showed only a slight decrease (2–3 wt%) after leaching, while SSA_1, SSA_2, and their carbonated counterparts exhibited a much larger reduction of about 10–20 wt%. This indicates that part of the amorphous fraction in SSA_1 and SSA_2 is soluble under strongly acidic conditions (pH ~1.6), whereas at the higher pH typical of SSA_3, the amorphous fraction remains essentially stable. Gypsum emerged as the most abundant crystalline phase in the leached ashes (Table 5), forming as a consequence of the reaction between Ca and S under strongly sulfate-rich conditions resulting from the use of H₂SO₄ as the leaching agent. The gypsum content was remarkably high in both treated and untreated samples: approximately 46 wt% for SSA_1, 48 wt% for SSA_2, and 60 wt% for SSA_3.

The efficiency of phosphorus extraction, both before and after carbonation (Table 4), appears to be strongly influenced by the amorphous content of the samples. As shown in Fig. 17, a clear correlation emerges, suggesting that phosphorus hosted in the amorphous fraction is more easily mobilized than that incorporated in crystalline phases. Although no direct evidence has been reported in the literature for SSA, it is known that a reduction in the crystallinity of hydroxyapatite enhances its dissolution rate [102]. This observation confirms that leaching effectively extracts phosphorus from the amorphous fraction, strongly suggesting that, in these samples, pH is not the only predominant factor governing phosphorus leachability. This strongly suggests that, in addition to optimizing the incineration operating conditions (e.g., furnace temperature), a careful control of the cooling regime of SSA after sludge combustion could significantly influence the amorphous fraction. By promoting higher amorphous content, it may be possible to improve both the efficiency of phosphorus recovery and the overall quality of the extracted product.

Table 5. Quantitative Phase Analysis of the as-collected SSA; R_{wp} is the refinement agreement factor; χ^2 is the goodness-of-fit statistic from the Rietveld refinement.

Crystalline phases			SSA_1 leached	SSA_1 CO ₂ leached	SSA_2 leached	SSA_2 CO ₂ leached	SSA_3 leached	SSA_3 CO ₂ leached
name	chemical formula							
anhydrite	$CaSO_4$		0.5 (1)	0.7 (1)	1.0 (1)	0.8 (1)	1.3 (1)	1.5 (1)
gypsum	$CaSO_4 \cdot 2H_2O$		46.5 (14)	47.9 (15)	47.8 (15)	48.1 (12)	63.95 (21)	59.5 (19)
calcite	$CaCO_3$		0.7 (1)	0.5 (1)	0.7 (1)	2.2 (2)	3.6 (2)	6.2 (3)
goethite	$FeO(OH)$		0.4 (1)	0.4 (1)	-	-	-	0.5 (1)
hematite	Fe_2O_3		11.1 (4)	10.3 (4)	10.1 (4)	9.6 (3)	3.9 (3)	3.9 (2)
whitlockite	$Ca_9Mg(PO_4)_7$		-	-	-	-	4.5 (2)	2.5 (1)
quartz	SiO_2	wt%	12.6 (3)	12.1 (2)	13.4 (3)	12.9 (3)	5.7 (3)	4.8 (2)
tridymite	SiO_2		2.3 (1)	2.6 (2)	4.3 (2)	5.1 (3)	1.9 (1)	3.6 (2)
albite	$NaAlSi_3O_8$		2.7 (1)	2.2 (2)	-	-	-	-
Mg- sulfate	$MgSO_4$		0.5 (1)	0.6 (1)	0.8 (1)	1.1 (1)	0.5 (1)	0.4 (1)
srebrodolskite	$Ca_2Fe_2O_5$		0.4 (1)	0.6 (1)	1.3 (1)	1.1 (1)	0.9 (1)	1.0 (1)
amorph			22.3 (7)	22.1 (4)	20.6 (8)	19.1 (7)	13.7 (5)	17.1 (7)
Cr. phosphorus	P						0.92	0.51
R_{wp}			2.83	2.39	2.96	3.06	3.02	3.07
χ^2			3.52	2.72	3.60	4.22	3.12	3.34

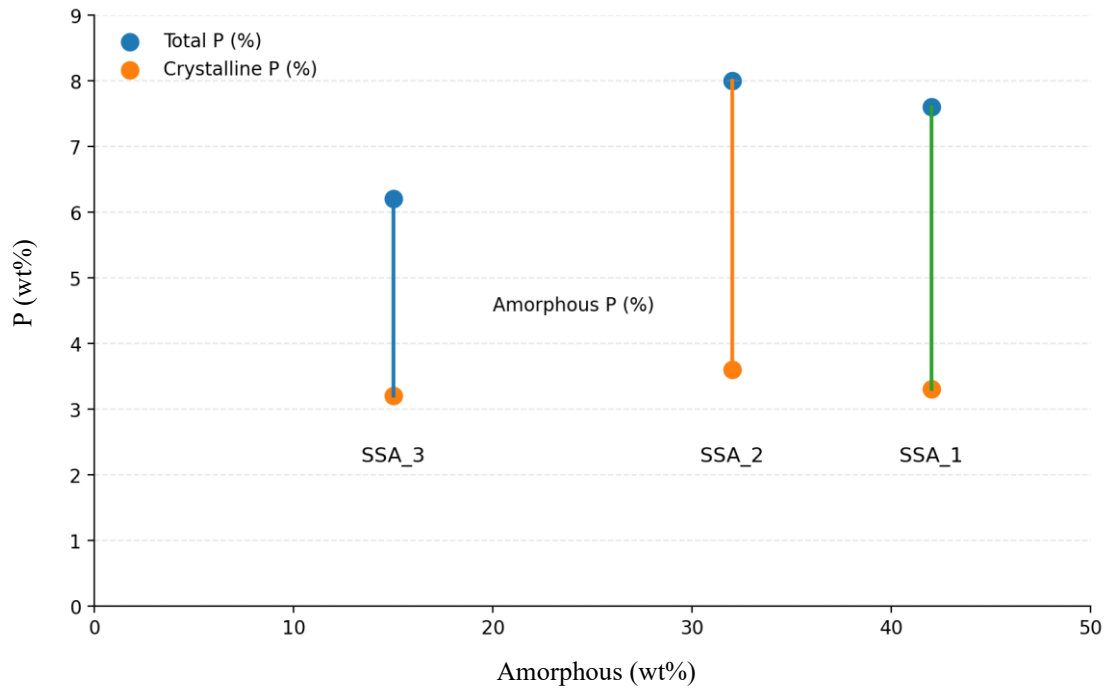


Figure 15. P concentration in the SSAs, evaluated by ICP-OES and P concentration evaluated through QPA analysis, plotted with the total amorphous content, also determined through QPA analysis.

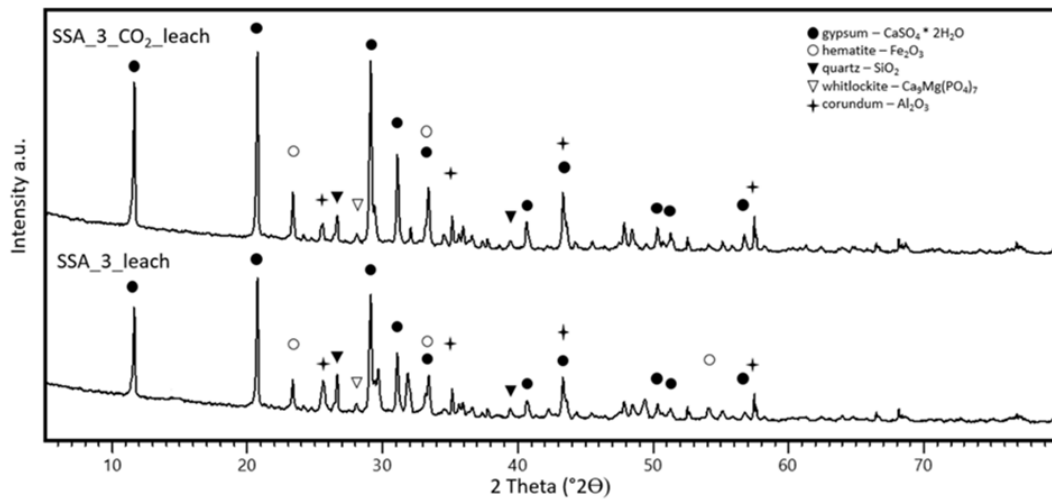


Figure 16. X-ray diffraction pattern of SSA_3_leach (bottom) and SSA_3_CO₂_leach (top).

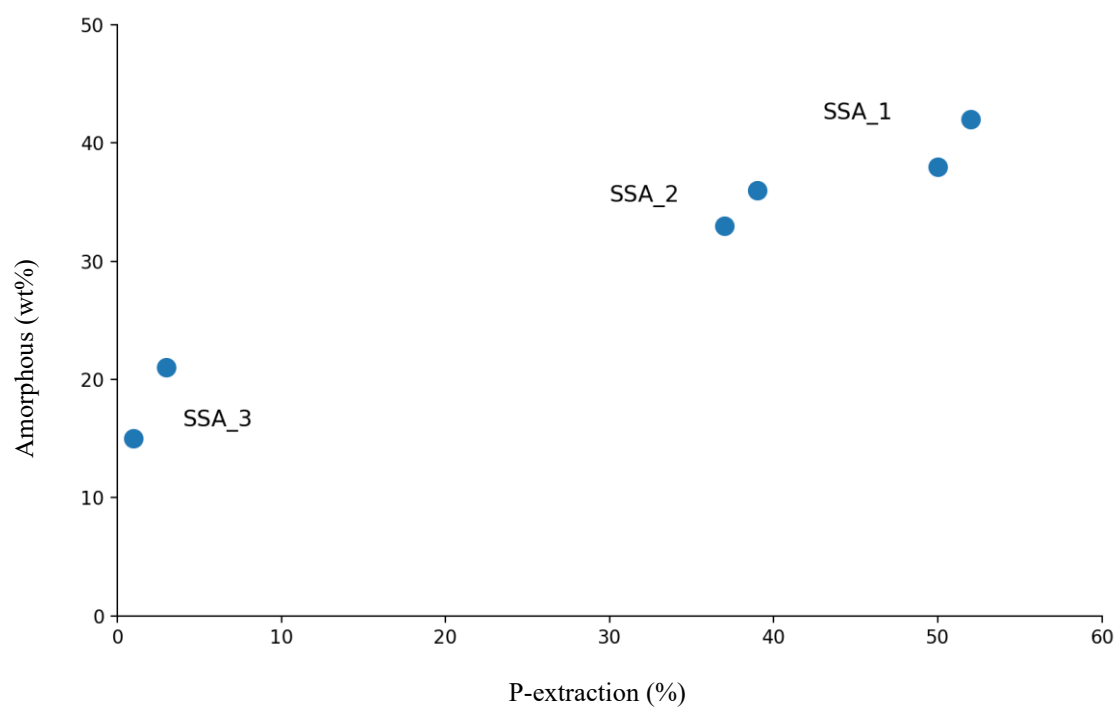


Figure 17. Extraction efficiency of the as collected and carbonated sample versus the total wt% of the amorphous phase.

2.4 Conclusions

Sewage sludge ash (SSA) samples were characterised by ICP-OES and X-ray diffraction with Quantitative Phase Analysis (after each step of the trial) to determine the total phosphorus (P) content and evaluate the crystalline and amorphous P-phases. The results revealed that P is predominantly hosted in the amorphous fraction, with smaller proportions incorporated into crystalline phases such as whitlockite, hydroxyapatite, tetrapotassium pyrophosphate (SSA_1 and SSA_2), and monetite (SSA_3).

Forced CO₂ carbonation trials were performed on all samples, leading to mineralisation processes on the surface of SSA particles. SEM-EDS analyses confirmed that partially decomposed Ca-bearing phases underwent a “restoration” process, characterised by the reappearance of crystal faces and the growth of newly formed CaCO₃ crystals at both nanometric and micrometric scales. Among the samples, SSA_3 showed the most favourable results, with an estimated CO₂ uptake of approximately 20 kg per ton of dry matter, highlighting its potential suitability for CO₂ mineralisation.

Carbonation also resulted in a reduction of SSA pH; however, the amount of P extracted using 0.2 M H₂SO₄ remained essentially unchanged, indicating that carbonation does not enhance P recovery through acid leaching. Instead, the results showed that P extraction efficiency is more strongly correlated with the amorphous content of SSA.

Overall, the process offers several advantages: CO₂ is permanently stored in a stable, non-leachable form; industrial waste is valorised in line with circular economy strategies, and the carbonated products can be reused in sectors such as construction, for instance, as supplementary cementitious materials. Nevertheless, optimization of key process parameters was beyond the scope of this study and should be addressed in future work to maximize CO₂ uptake. Taken together, the results suggest that SSA carbonation could represent a promising approach to mitigate CO₂ emissions.

Acknowledgements

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3. In-Depth Characterisation of Sewage Sludge Ash and Microwave-Assisted Thermochemical Process for Crystalline Phase Evolution

Building upon the results obtained from wet extraction and carbonation processes, which highlighted the limitations associated with the intrinsic stability of phosphorus-bearing phases in sewage sludge ash (SSA), this chapter focuses on thermochemical strategies to overcome these constraints.

As discussed, the mineralogical nature of P-bearing crystalline phases plays a fundamental role in determining their reactivity and extractability. In SSA, phosphorus is mainly incorporated into stable phases such as whitlockite and hydroxyapatite, limiting the effectiveness of conventional acid leaching.

To better understand these limitations, a more in-depth characterisation of SSA is performed, with particular attention to particle-scale analysis using SEM–EDS. This approach reveals that phosphorus may remain physically trapped within the heterogeneous matrix, reducing its accessibility and extraction efficiency.

To address this issue, a microwave-assisted thermochemical treatment in the presence of alkaline additives is proposed to induce controlled phase transformations and promote the formation of more reactive or soluble phosphorus-bearing phases. This is coupled with leaching in neutral ammonium citrate, enabling a more sustainable process and the potential direct applicability of the resulting solutions in agricultural contexts. Particular emphasis is placed on the identification and quantification of the crystalline phases formed and their influence on phosphorus solubilization behaviour.

Abstract

This study investigates the chemical, crystalline and particle composition of a complex matrix, the sewage sludge ashes (SSA) posing a particular focus on the P-bearing phases. Moreover, it investigates the thermochemical transformation of phosphorus (P) in sewage sludge ash (SSA) through microwave-assisted treatment using sodium bicarbonate (NaHCO_3) and potassium bicarbonate (KHCO_3), aiming to enhance P availability. Two SSA samples, characterised by high iron content and complex mineralogy, were treated at 800 and 1000 °C and subsequently evaluated through XRPD-QPA, SEM-EDS, and leaching tests in neutral ammonium citrate (NAC). The as-collected SSAs exhibited a heterogeneous structure with significant amorphous

content (35–46 wt%), where phosphorus is mainly associated with Ca–Mg phosphates (e.g., whitlockite) and partly embedded in Fe–Si-rich matrices, limiting its extractability. NAC leaching confirmed low P recovery ($\approx 20\text{--}23\%$), highlighting the refractory nature of the untreated material. Microwave thermochemical treatment induced substantial phase transformations. In NaHCO_3 -treated samples, phosphorus was predominantly converted into buchwaldite (NaCaPO_4), with crystalline P increasing to $\approx 5\text{ wt}\%$ and extraction efficiencies reaching up to $\approx 100\%$ at $800\text{ }^\circ\text{C}$. SEM-EDS revealed the formation of well-defined phosphate blebs segregated from the silicate matrix and iron oxides, indicating effective phase separation and enhanced solubility. In contrast, KHCO_3 treatment resulted in partial transformation to KCaPO_4 , with residual whitlockite and hydroxyapatite, reflecting limited reactivity and incomplete P conversion. Overall, NaHCO_3 demonstrated superior fluxing behaviour, promoting extensive melting, recrystallisation, and phosphorus redistribution into highly soluble phases.

The results highlight the potential of microwave-assisted thermochemical processing as an efficient strategy for phosphorus recovery from SSA, with process performance strongly dependent on the selected alkaline additive and treatment temperature.

Keywords: Sewage Sludge Ashes, MW-treatment, P-secondary sources, P-bioavailability in SSA, Buchwaldite, KCaPO_4

Scientific contribution

The content presented in this chapter is the result of original work, including literature review, data curation, formal analysis, investigation, methodology development, conceptualization, and writing. In this section, the thermochemical process is described in greater detail, providing a comprehensive discussion of its underlying mechanisms, as well as its main advantages and limitations.

The results discussed in this chapter, although obtained through a different methodological approach, contributed to the development of the following publication:

- Calce S, Massa M, Valentim B, Punta C, Pachaiappan P, Mannu A, et al. Sustainable phosphorus recovery from sewage sludge ash through microwave-assisted thermochemical treatment for next-generation fertilizers. *J Clean Prod* 2026;555:148167. <https://doi.org/10.1016/j.jclepro.2026.148167>.

however, the material has been revised and deeply expanded in order to ensure consistency with the structure and scope of this doctoral thesis.

3.1 Introduction

Municipal wastewater treatment plants represent one of the most significant anthropogenic reservoirs of phosphorus [103]. During wastewater treatment, a large fraction of the phosphorus consumed by human activities is transferred to sewage sludge (SS). When sewage sludge undergoes mono-incineration, sewage sludge ash (SSA) is produced as a mineral residue that can be enriched in phosphorus. However, as reported in the literature, the phosphorus content can vary widely, typically ranging from 0.6 to 12 wt%, resulting in significant variability among SSA materials. This heterogeneity makes SSA an inconsistent and potentially unreliable source of phosphorus. [104]. From a materials science perspective, SSA can be described as a complex multiphase oxide and elemental system primarily composed of Ca–Fe–Al–Mg–Si but accompanied by several elements such as K, Na, Cr, Zn, Cu, Pb, Ni, Cd and As [61] [105] [106] [107] [108] [109] [110] [111].

Phosphorus is mainly incorporated within whitlockite-type solid solutions, $\text{Ca}_{3-x}(\text{Mg,Fe})_x(\text{PO}_4)_2$, and occasionally within hydroxyapatite [112] [80]. The limited agronomic availability of phosphorus in SSA is therefore not simply related to its overall concentration but is largely controlled by the crystallographic environment and thermodynamic stability of these P-bearing phases. Any strategy aimed at enhancing phosphorus reactivity must therefore address the mineralogical constraints imposed by the high-temperature incineration process.

As discussed in the previous chapter, acid extraction using 0.2 M sulfuric acid leads to maximum extraction efficiencies of about 52.1%, although much lower values—sometimes below 1%—can be observed when the system exhibits a high buffering capacity due to the presence of $\text{Ca}(\text{OH})_2$ [113]. Wet extraction processes rely on the dissolution of phosphate phases using mineral or organic acids; however, the dissolution behaviour is strongly influenced by phase composition and often results in the simultaneous co-extraction of heavy metals [101]. Consequently, the efficiency and selectivity of hydrometallurgical recovery are intrinsically limited by the mineralogical stability of the ash. In addition, the use of acidic reagents generates secondary waste streams that must be properly managed after phosphorus has been recovered, typically as precipitated phosphate products [114].

Thermochemical treatments provide an alternative route, as explored in Section 1.5, operating through solid-state transformations that modify the structural environment of phosphorus prior to dissolution or potential reuse. However, the mechanisms governing these transformations at the microscale, as well as the formation and quantification of the resulting crystalline phases,

have rarely been investigated in detail. To date, only limited studies have addressed this aspect, highlighting a significant gap in the understanding of phase evolution during thermochemical processing [112].

Despite their effectiveness, many thermochemical treatments are considered highly energy demanding, which represents a relevant limitation for large-scale implementation [115]. Nevertheless, these processes share a common mechanistic principle: the destabilization of the original phosphate phases present in SSA and the formation of new crystalline environments characterised by different thermodynamic and kinetic properties. In particular, partial substitution of Ca^{2+} or Mg^{2+} by alkali ions such as Na^+ or K^+ may lead to the formation of Ca–alkali phosphates, including buchwaldite (NaCaPO_4) or KCaPO_4 [112]. The higher NAC solubility observed for these phases is closely related to their modified crystal chemistry and lattice energy.

More recently, increasing attention has been directed toward alternative energy inputs for thermochemical activation. Microwave heating at 2.45 GHz provides volumetric and selective heating through dipolar polarization and ionic conduction mechanisms, allowing rapid temperature increase and potentially different reaction pathways compared to conventional radiative–convective heating. Although microwaves do not directly break chemical bonds, their interaction with dielectric materials can enhance reaction kinetics through localized heating and reduced thermal gradients. Previous studies have demonstrated the feasibility of microwave-assisted carbothermic reduction in complex oxide systems, as well as the formation of NaCaPO_4 from SSA under hybrid microwave conditions [112] [80].

Within this framework, thermochemical treatment can be interpreted not only as a recovery technology but also as a phase-engineering strategy applied to complex multicomponent oxide systems. The objective is to control solid-state reactions, cation diffusion, and phase equilibria in order to reconstruct the crystallographic environment of phosphorus and consequently modify its chemical reactivity.

The present work investigates the microwave-assisted thermochemical treatment of SSA using sodium- and potassium-based additives in the temperature range of 800–1000 °C. Operating at temperatures lower than those typically employed in pyrometallurgical processes allows targeted phase transformations while limiting the overall energy demand. Particular attention is devoted to the mineralogical and microstructural evolution of the ash before and after treatment. By correlating phase composition, crystallographic modifications, and dissolution behaviour in neutral ammonium citrate, this study aims to elucidate the relationship between solid-state transformation mechanisms and phosphorus reactivity.

Rather than focusing exclusively on phosphorus recovery efficiency, this study considers thermochemical processing as a tool to modify the stability and solubility of P-bearing phases within complex Ca–Fe–Mg–Si oxide matrices. The central hypothesis is that phosphorus availability is governed by its structural incorporation within the mineral framework, and that controlled phase reconstruction can be achieved through tailored thermochemical activation. In addition, the solubility behaviour of the main nutrients and contaminants typically present in SSA will be evaluated before and after thermochemical treatment. Among the macronutrients considered are P, Na, Mg, K, and S, while the contaminants include heavy metals such as Cu, Ni, Cr, Zn, and Pb. Finally, this section discusses the importance of phosphorus recovery from secondary sources and the potential role of advanced thermochemical technologies in securing future phosphorus supplies while minimizing environmental impacts. In this context, the proposed approach aims to contribute to the development of processing strategies that move toward a zero-waste management of phosphorus-containing residues

3.2 Experimental

3.2.1 Materials

Two samples of SSA, employed for the thermochemical treatment, were obtained from the mono-incineration of SS in a fluidized bed combustion chamber at a temperature of 850 °C, using silica sand as the bedding material. Sample SSA_1 comes from the mono-incineration of dewatered sludge pellets, while sample SSA_2 is a mixture of thermally dried and dewatered sludge pellets. Both samples originate from a treatment process characterised by intensive chemical phosphorus removal, involving high FeCl_3 dosage and limited biological P removal. Consequently, the ashes contain elevated iron levels, imparting a characteristic reddish coloration. Figure 18 shows the 2 samples of SSA.

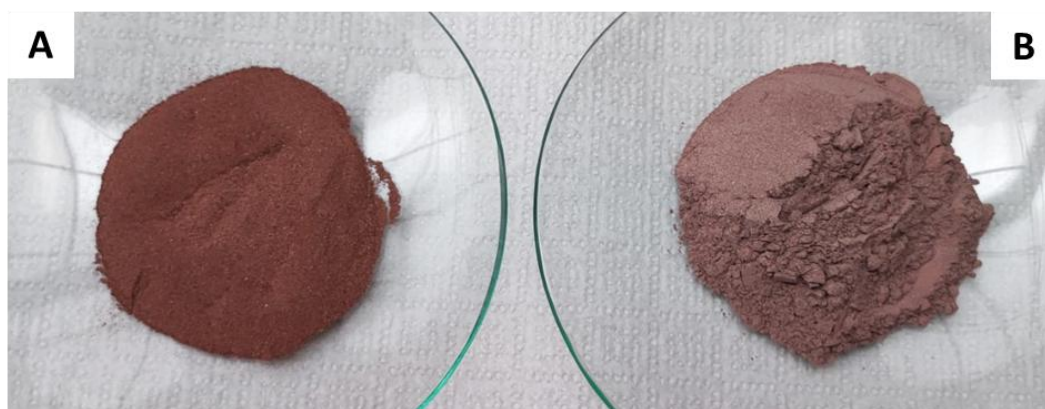


Figure 18. SSA_2 (A) with a coarser particle size and SSA_1 (B) with a finer particle size, both display the characteristic red colour due to the high presence of Fe.

The SSAs have been ground and homogenized with a Retsch MM400 ball mill in a 50-mL iron jar with three iron spheres having a diameter of 15 mm (frequency 30/s for 3 min) to obtain a fine powder. The powder was later mixed with two different reagents: sodium bicarbonate (NaHCO_3 – CAS 144-55-8) and potassium bicarbonate (KHCO_3 – CAS 298-14-6), purchased from Sigma-Aldrich both with a purity $\geq 99.7\%$, according to a recipe of 70 wt% SSA and 30 wt% reagent. The powders mixture was homogenized inside a falcon tube on a vortex, vibrating for five minutes. A fraction of the powder was used to produce tablets of about 5 g with a hydraulic press at 300 bar for three minutes.

The neutral ammonium citrate (NAC) was prepared according to the procedure [116] [117]: 370 g of pure crystallized citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ – CAS 5949-29-1, purity $\geq 99\%$ purchased by Sigma-Aldrich) is dissolved in about 1.5 L of water, then partially neutralized by gradually adding 345 mL of ammonia solution (29% of NH_3 -CAS 1336-21-6, purchased by Sigma-

Aldrich). The solution is then cooled and carefully brought to exact neutrality (pH 7.0 at 20 °C), using a pH meter and adding the ammonia solution dropwise under continuous stirring. The solution is diluted to a final volume of 2 L, the pH is verified, and the reagent is stored in a tightly sealed container, with periodic pH checks.

3.2.2 Microwave Thermochemical Treatment

The thermochemical treatment was performed using a PYRO Advanced Microwave Muffle Furnace (Milestone S.r.l., Bergamo, Italy). The system operated under an air atmosphere with a constant flow rate of 45 m³/h and a maximum power of 1500 W, with self-adjusting output according to the programmed temperature and duration. Treatments were carried out at two target temperatures: 800 °C and 1000 °C, with a heating rate of approximately 45-50 °C/min. The MWs are directed at a silicon carbide (SiC) susceptor able to quickly absorb them, heating the chamber in a short time. The microwave absorption efficiency of the susceptor decreased with increasing temperature. This trend was confirmed by the power–temperature profiles (Figure 19), which demonstrated that as the furnace temperature increased steadily, the applied power also rose accordingly.

Each treatment (Figure 19) consisted of two steps:

- 1) a heating phase to reach the set final temperature;
- 2) an isothermal stage of 20 minutes, applied at each investigated temperature, to assess the exchange reaction between the SSA and the two reagents.

3.2.3 Acid Digestion and Wet Extraction with Neutral Ammonium Citrate (NAC)

The samples were finely powdered, using a ball mill as previously described (section 3.1.1), before the acid digestion (performed as in section 2.2.2 - 1 g in 100 mL of aqua regia) and leaching with NAC on the sample after the MW-treatment. The extraction of P with NAC was performed by transferring 1 g of MW-treated SSA into a 200–250 mL flask containing 100 mL of ammonium citrate solution, pre-heated to 65 °C. The flask was tightly shaken to disperse the sample in suspension, avoiding the formation of lumps, and then briefly opened to release excess pressure, then resealed. The flask was placed in a water bath maintained at 65 °C, maintaining the suspension level in the flask below the water level in the bath. The sample was stirred, keeping the powder constantly in suspension for one hour, then removing the flask from the bath and cooling it under running water to room temperature. The content was transferred into a calibrated 500 mL volumetric flask using a wash bottle, diluted to volume with water,

homogenized, and filtered into a clean dry container, discarding the first ~50 mL of filtrate and saving the solid residue for further analysis.

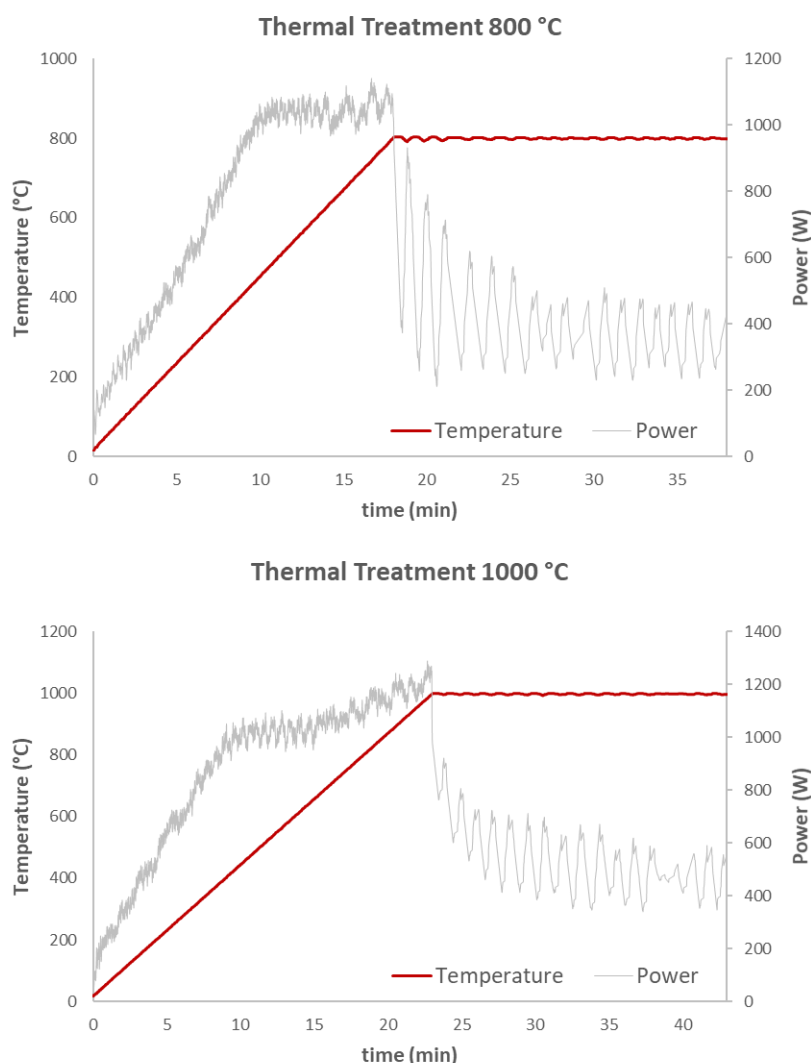


Figure 19. Thermal Treatments with Temperature and Power paths; 800 °C (up) and 1000 °C (down).

3.2.4 Characterisation Techniques of as-collected and MW-treated Samples

3.2.4.1 Analyses of the Solutions Through Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Total Reflection X-ray Fluorescence Spectroscopy (TXRF), Spectrophotometry UV-Vis

ICP-OES analysis was conducted on the digested, MW-treated, and NAC-leached samples with the same instrument and procedure followed in section 2.2.4.3 on P and other elements, including the major macronutrients such as calcium (Ca), magnesium (Mg), sodium (Na),

potassium (K), sulfur (S) and one of the heavy metals (Cd) non quantifiable through TXRF analysis.

Elemental analysis was performed using a benchtop TXRF spectrometer (Horizon, G.N.R., Italy). The system is equipped with a molybdenum X-ray tube and a W/Si multilayer monochromator, generating a Mo-K α excitation beam at 17.44 keV. Fluorescence signals were collected using a 40 mm² Silicon Drift Detector (KETEK GmbH) fitted with a 1 mm graphene window, collimator, and polymeric foil. Measurements were performed in air at 40 kV and 15 mA, with a counting time of 600 seconds. Samples have been properly diluted with Milli-Q water. A gallium solution ($\approx$ 500 mg/kg) was used as an internal standard to quantify the following elements: chromium (Cr), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), lead (Pb), and arsenic (As); The 10 μ L of the solutions were dried on a plexiglass sample holder and dried at 60 °C in a closed vessel. Three replicates of the dried samples were analysed.

Both ICP-OES and TXRF analyses were repeated three times on each sample to ensure data replicability.

The concentration of Cr⁶⁺ in the solution was measured by the spectrophotometer Hach Lange DR 3800 at the wavelength of maximum absorption (653 nm), working with the chromium/chromium (VI) cuvette test

LCK 313 (0.03 to 1mg/L of Cr (VI)), also manufactured by Hach. To avoid interference from other elements found in the sample, it was leached in water with an L/S ratio of 10 (e.g., 1 g - 10 mL of Milli-Q water), following the procedure for Cr (VI) quantification.

3.2.4.2 Analyses of Solid Samples with X-ray Powder Diffraction (XRPD) and Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS).

The XRPD and SEM-EDS analysis was carried out on the as-collected, MW-Treated, and solid residue (SR) after the NAC-leaching test. The XRPD, according to the procedure explained in section 2.2.4.1, with the internal standard to perform the QPA, but only when possible: the MW-Treated and NAC-leached samples involving KHCO₃ generate compounds like KCaPO₄ with a crystallite structure not yet solved [118]. The acquisition was made in a range of 10 – 90 °2Theta with a step size of 0.02 °2Theta.

The SEM-EDS acquisitions were performed at the Materials Centre of the University of Porto (CEMUP, Portugal), as explained in Section 2.2.4.2, using the same instrument configuration and also a different sample preparation method. As-collected samples and MW-treated samples were analysed in powder on the carbon tape and polished using 5 g of powder and a vertical

section of the tablet, respectively. The samples were embedded in a cylindrical cast with resin and hardening liquid (ratio = 1/5), then cut into two half-blocks to polish the internal surface. The smoothing was achieved using a SiC abrasive polishing material, specifically P220, P360, P600, P1000, and P4000 (decreasing grain size from $\approx$ approximately 60 μm to $\approx$ approximately 5 μm), followed by two final stages with Al_2O_3 solutions of 1 μm and 0.1 μm grain size. Samples were finally cleaned with a sonic water bath to remove the Al_2O_3 solution residues. The SRs were the only ones analysed in the form of powder to detect pattern changes due to the structure's dissolution. Both the powdered samples and the polish blocks have been sputtered with a carbon film before the SEM-EDS acquisition.

3.3 Results and Discussion of the as-collected Sewage Sludge Ashes

3.3.1 Chemical analysis, XRPD-QPA, and SEM-EDS

The data were collected on the digested SSAs and after the NAC-leaching with ICP-OES, TXRF, and spectrophotometry UV-Vis for Cr (VI) results.

The concentration of the elements for the digested samples is reported in Table 6. The total amount of P is about 67.000 mg/kg and 59.000 mg/kg for SSA_1 and SSA_2, respectively. The elements considered macronutrients according to the EU 2019/1009 and present in the following concentrations: Ca $\approx$ 120.000 – 14.5000 mg/kg, S $\approx$ 12.000 – 18.000 mg/kg, Mg $\approx$ 9.000– 12.000 mg/kg, K $\approx$ 5.000 mg/kg, Na $\approx$ 1.000 mg/kg. The HMs are reported in Table 7. Analyses revealed that all the HMs are in higher content compared to the legislation limits, especially Zn ($\approx$ 4.000 mg/kg), Ni ($\approx$ 1.000 mg/kg), and Cu ($\approx$ 1.000 mg/kg). The only values below the limits are Cr (Vi) (Total Cr $\approx$ 400 mg/kg), Cd for both samples, and As for SSA_1 ($\approx$ 25 mg/kg). The results include titanium (Ti) and iron (Fe), which are not listed among the contaminants but present in high amounts (Fe $\approx$ 180.000 mg/kg), with iron being the major element of the ashes.

Table 6. Chemical analysis of digested SSA_1 and SSA_2 and the detection limit for each element. Elements marked by * collected with TXRF, analyses for Cr (VI) with UV-vis.

Sample	Digested						Detection
	SSA_1			SSA_2			limit
Element	mg/kg						mg/L
P	67302	±	5268	59177	±	5310	0.05
Na	1717	±	132	1312	±	133	0.01
K	4792	±	132	4282	±	133	0.01
Ca	143298	±	2634	120000	±	2655	0.01
Mg	11182	±	527	9319	±	531	0.05
S	17470	±	1317	12133	±	1327	0.1
Cd	52	±	3	43	±	3	0.001
Ti*	7992	±	1615	6200	±	587	0.01
Cr*	478	±	30	405	±	8	0.007
Cr (VI)	< LOQ						0.03
Fe*	192870	±	8902	177187	±	2513	0.004
Ni*	1037	±	398	1311	±	12	0.003
Cu*	1117	±	47	1496	±	22	0.002
Zn*	4188	±	386	4173	±	36	0.002
Pb*	364	±	59	405	±	55	0.008
As*	25	±	9	46	±	13	0.002

X-ray and QPA data are reported in Table 8 and the diffraction pattern of the Rietveld refinement plots in Figures 20 (SSA_1) and 21 (SSA_2). The QPA analysis revealed a very heterogeneous set of compounds, a crystalline structural resemblance, and a high amorphous content (34.7 wt% SSA_1 and 46.3 wt% for SSA_2) between the two samples. P is contained in three crystalline phases, $\text{Ca}_9\text{Mg}(\text{PO}_4)_7$ (main P-bearing phase) in high content 11,3 wt% and 7,3 wt% for SSA_1 and SSA_2, respectively, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (≈ 3.5 wt%) and $\text{K}_4\text{P}_2\text{O}_7$ (≈ 0.7 wt%). Crystalline P is quantified at 3.25 wt% (SSA_1) and 2.11 wt% (SSA_2), and as in the previous chapter (n. 2), the majority of it ($\approx 50\%$ for SSA_1 and $\approx 65\%$ for SSA_2) is contained in the amorphous fraction. The major crystalline phases are CaCO_3 , CaSO_4 , and Fe_2O_3 , reflecting the high chemical content of these three elements. The other phases, mainly composed of Ca, Si, and Fe, are all contained in quantities of less than 2 wt%.

Table 7. QPA on the as-collected SSA and total crystalline P. R_{wp} is the refinement agreement factor; χ^2 is the goodness-of-fit statistic from the Rietveld refinement. $Tr < 0.1$ wt%.

Crystalline phases		SSA_1	SSA_2
name	chemical formula		
albite	$Na(AlSi_3O_8)$	1.9 (1)	0.2 (1)
anhydrite	$CaSO_4$	7.0 (1)	4.2 (1)
barite	$BaSO_4$	0.3 (1)	0.2 (1)
calcite	$CaCO_3$	9.3 (2)	12.4 (2)
calcium chloride hydroxide	$CaCl(OH)$	2.0 (1)	Tr
cristobalite	SiO_2	1.3 (1)	1.8 (1)
goethite	$FeO(OH)$	1.0 (1)	0.8 (1)
hematite	Fe_2O_3	8.7 (1)	6.9 (1)
hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	4.2 (1)	2.9 (1)
lime	CaO	Tr	Tr
magnesium sulfate	$MgSO_4$	0.2 (1)	0.5 (1)
monazite	$REE(PO_4)$	Tr	Tr
pigeonite	$(Mg,Fe,Ca)_2Si_2O_6$	2.1 (1)	1.1 (1)
portlandite	$Ca(OH)_2$	1.1 (1)	Tr
quartz	SiO_2	11.1 (2)	11.9 (3)
srebrodolskite	$Ca_2Fe_2O_5$	0.9 (1)	1.3 (1)
sulfur	S_8	1.2 (1)	0.6 (1)
K ₄ - pyrophosphate	$K_4P_2O_7$	0.8 (1)	0.6 (1)
tridymite	SiO_2	0.9 (1)	1.0 (1)
whitlockite	$Ca_9Mg(PO_4)_7$	11.3 (3)	7.3 (3)
amorphous		34.7 (7)	46.3 (7)
Cr. Phosphorus	P	3.25	2.11
R_{wp}		2.02	2.43
χ^2		1.79	2.70

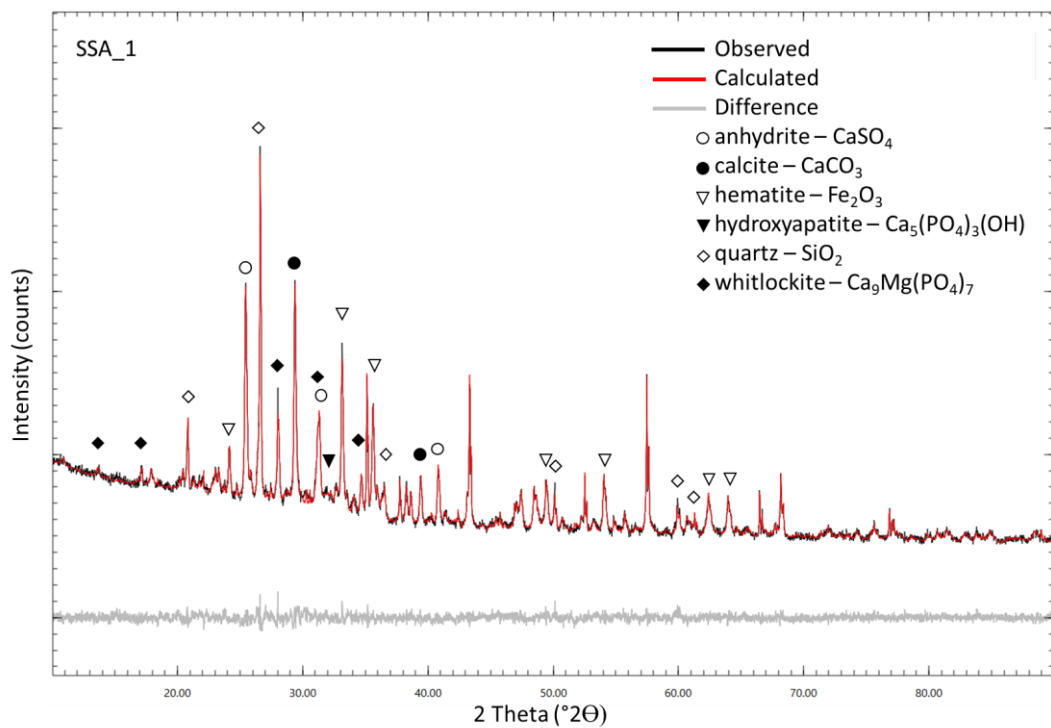


Figure 20. Diffraction pattern of the QPA for SSA_1, reporting the major crystalline phases.

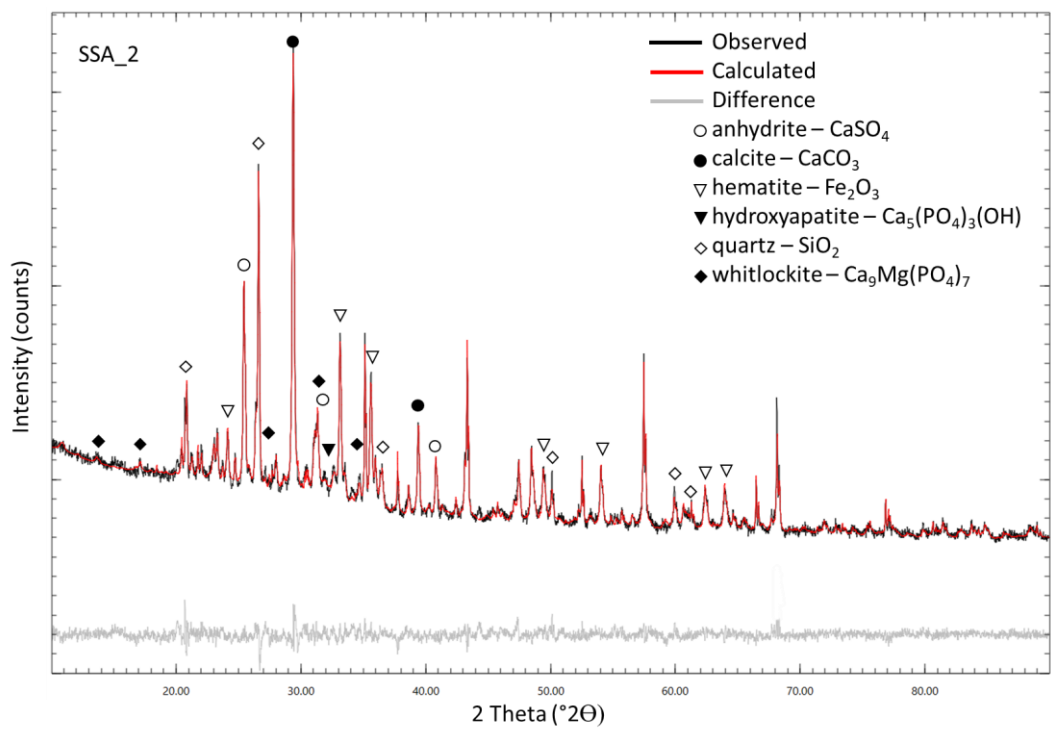


Figure 21. Diffraction pattern of the QPA for SSA_2, reporting the major crystalline phases.

SEM-EDS analysis proved to be an effective technique for characterizing this complex matrix with pronounced crystalline heterogeneity, while also providing valuable insights into the formation of crystals and phosphorus-bearing particles. Figure 22 shows the SEM micrographs with the corresponding EDS analysis zones (Z1, Z2, etc.), and Table 10 reports the results of the semiquantitative EDS analyses. Overall, the powders are characterised by particles of varying shapes and sizes (Figure 22A).

The data are mainly focused on phosphorus-bearing particles, which were classified into 3 main categories:

- *Phosphorus–silicon–iron Spheres (P–Si–Fe spheres)* (Figure 22B, E and F): these particles with a dimension of 30-100 μm were probably formed by the solidification of molten material and are characterised by an outer shell composed of iron oxide (spectrum Z11 - Figure 22F). The inner part, on the other hand, shows a highly complex association of elements (spectrum Z3) with a moderate-defined crystalline structures. In Figure 22E, spectrum Z7 (dark grey colour) exhibits Si-O content; Z8 (white colour) Fe-O content; Z9 and Z10 mainly Ca-P-O content.
- *Partially baked particles (PBP)* (Figure 22C): these particles with a wider range dimension (20 – 250 μm) exhibit a poorly defined structure as a consequence of thermal degradation inside the combustion chamber. Within this structural disorder, well-defined connections with clay minerals (detected by QPA) phases can be identified, along with localized regions enriched in Fe and P (spectrum Z4). PBP particles are mainly found in SSA_2, according with a higher wt% of amorphous phase characterising the sample.
- *Accretion P-Ca-Fe rims* observed on quartz (SiO_2 - Qz) particles (Figure 20D) coming from the silica sand employed as bed material during sewage sludge combustion. These particles are less present with a general dimension of $\approx 100\text{-}150$ μm . The shape and the layered structure appear like a stratification of poor crystalline material enriched in P-Ca-Fe on SiO_2 particles.

In Figure 22B, in addition to the phosphorus-containing particles, a SiO_2 crystal and a structure with a Ca–S–O composition (CaSO_4 and CaCO_3) are also shown.

Table 8. EDS semi-quantitative elemental analysis of SSA-1 and SSA_2 (Z6).

Acquisition	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9	Z10	Z11
Element	wt %										
C	9.4	6.1	6.4	11.5	9.9	6.8	6.7	2.8	5.8	6.1	5.1
O	39.5	33.6	29.6	23.6	33.8	28.2	39.3	20.6	29.0	28.7	22.6
P	-	-	14.8	17.6	-	14.1	-	0.4	19.0	22.1	1.6
Ca	43.9	-	10.1	0.7	-	19.7	-	0.6	31.9	34.1	1.0
Na	-	0.5	-	-	0.4	-	-	-	0.3	0.4	-
Mg	-	-	1.4	0.6	0.7	1.1	-	-	1.0	1.6	-
K	-	14.7	1.5	0.7	9.4	1.2	-	-	-	0.8	0.5
S	5.5	-	-	-	-	-	-	-	0.7	-	-
Al	0.8	9.8	3.2	-	18.1	1.7	0.8	0.5	0.4	0.6	1.3
Si	1.0	35.2	9.4	-	25.1	5.3	53.2	1.7	4.7	1.0	1.8
Fe	-	-	22.5	45.3	2.4	22.1	-	71.6	7.2	4.6	64.6
Ti	-	-	-	-	-	-	-	1.9	-	-	1.5

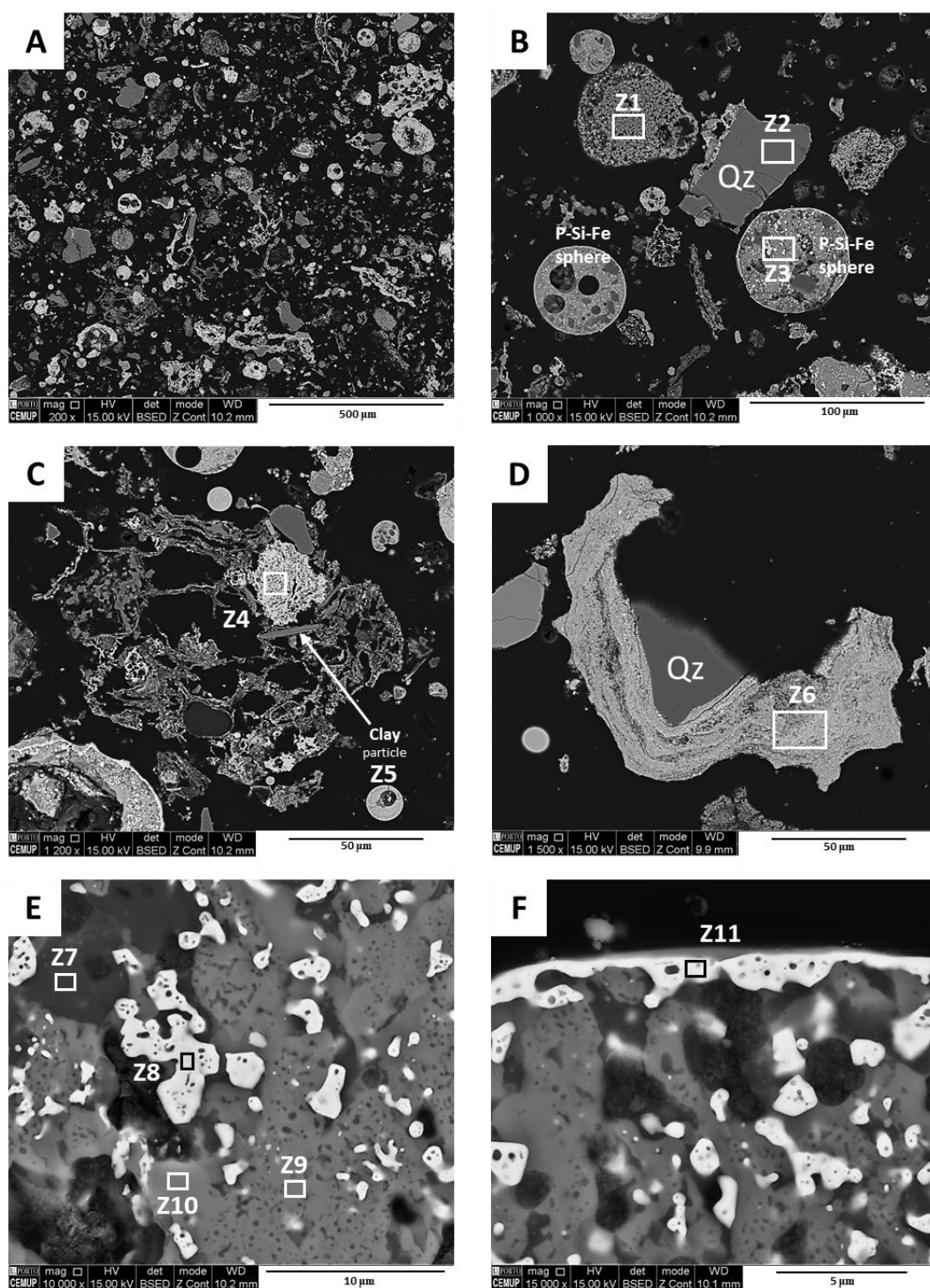


Figure 22. SEM-EDS analyses of as-collected SSA particles: (A) low magnification of SSA (sample SSA_2; BSE mode; 200 $\times$); (B) Phosphorus-silicon-iron Spheres (P-Si-Fe spheres) and spectra Z1-Z2_Z3 (sample SSA_1; BSE mode; 1,000 $\times$); (C) Partially baked particles (PBP), spectra Z4-Z5 (sample SSA_2; SE mode; 1,200 $\times$); (D) Accretion P-Ca-Fe rims observed on quartz, spectra Z6 (SiO_2 - Qz) particles (sample SSA_1; BSE mode; 1,500 $\times$); (E) high magnification of the internal structure of a P-Si-Fe spheres, spectra Z7-Z8-Z9-Z10 (sample SSA_1; BSE mode; 10,000 $\times$); (F) high magnification of

the internal structure of a P–Si–Fe spheres with a focus on the outer iron shell, spectra Z11 (sample SSA_1; BSE mode; 10,000×).

Figure 23 presents four additional SEM-EDS micrographs of less common structures. In Figure 23A, a fragment approximately 30 µm thick is observed, consistent with a bone particle and characterised by a chemistry dominated by Ca and P, thus identified as hydroxyapatite (Table 9). Figure 23B shows a small crystal with a high Ba and S content (Table 9), corresponding to barite detected through XRD. In Figure 23C, a particle composed of Zn, Ni, and Cr oxides is displayed, highlighting the presence of HMs detected by TXRF. Finally, Figure 23D depicts a particle containing P associated with cerium (Ce) and lanthanum (La), a structure probably similar to monazite, which was identified in trace amounts through QPA.

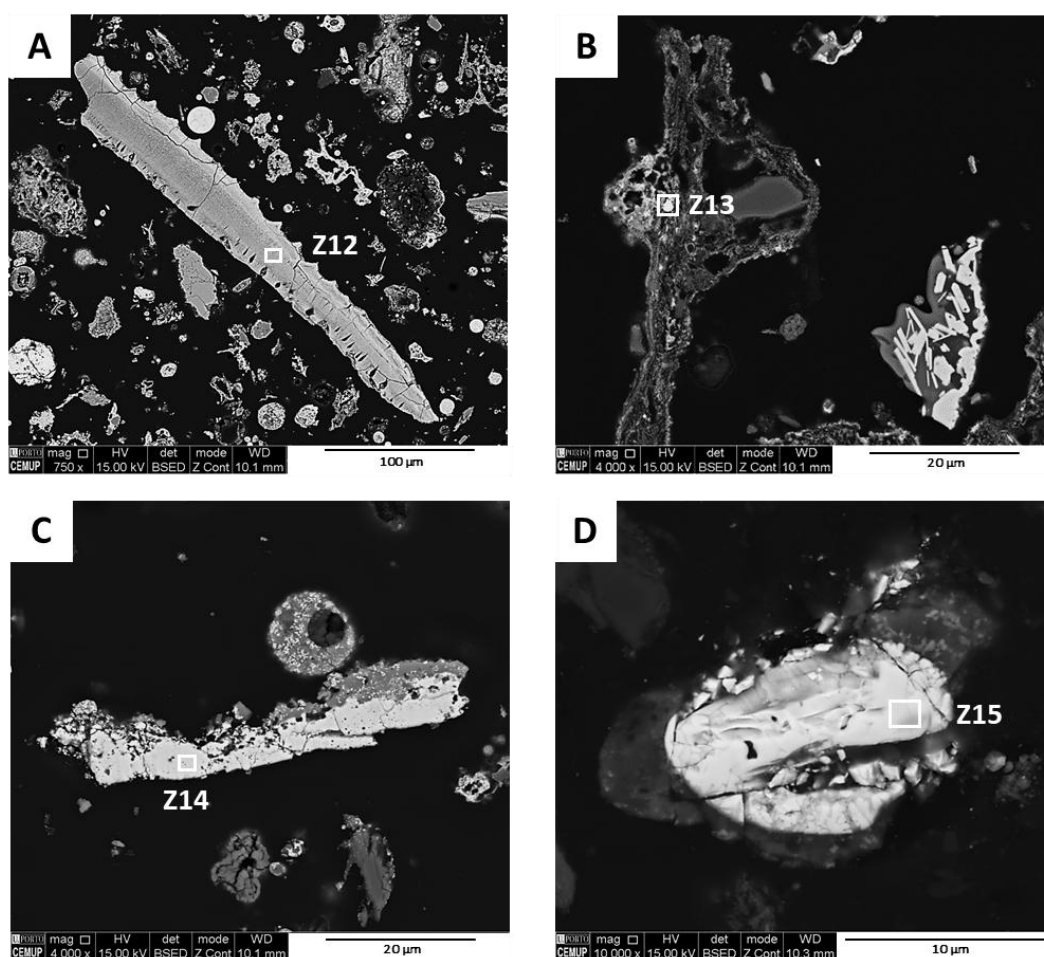


Figure 23. SEM-EDS analyses of as-collected SSA particles: (A) bone residue made in Ca and P, most likely hydroxyapatite and spectra Z12 (sample SSA_1; BSE mode; 750×); (B) barite crystal embedded in a PBP particle and spectra Z13 (sample SSA_1; BSE mode; 4,000×); (C) Particle containing Cr-Ni-Zn and spectra Z14 (sample SSA_2; SE mode; 4200×); (D) Particle containing Ce-La and P probably a monazite crystal and spectrum Z15 (sample SSA_2; BSE mode; 10000×).

Table 9. EDS semi-quantitative elemental analysis of SSA-1 and SSA_2 (Z13).

Acquisition	Z12	Z13	Z14	Z15
Element				
C	13.9	7.2	4.1	2.1
O	24.8	18.4	17.1	8.2
P	16.5	3.8	-	6.2
Ca	34.3	3.8	0.5	-
Mg	-	0.3	-	-
K	-	0.4	-	-
S	-	9.8	-	-
Al	-	0.6	0.6	-
Si	-	1.8	0.4	-
Fe	9.0	4.2	38.0	2.4
Ti	-	-	-	-
Zn	-	-	2.7	-
Ni	-	-	24.9	-
Cr	-	-	11.8	-
Cl	1.4	-	-	-
Ba	-	49.9	-	-
Ce	-	-	-	51.6
La	-	-	-	29.5

3.3.2 Sewage Sludge Ash as a Secondary Resource for Phosphorus Recovery and Its Potential Use in Agricultural Applications

The two SSAs under investigation can be regarded as a highly complex matrix, as demonstrated by chemical analyses, XRPD-QPA, and SEM-EDS. The noteworthy content of P and other potential macronutrients (Ca, S, Mg, K, and Na) is accompanied by elevated concentrations of heavy metals, as well as by the exceptionally high Fe content, which is introduced upstream during wastewater treatment before incineration (as described in Chapter 2). The main structures identified by QPA and SEM-EDS consist of phosphates, sulfates, silicates, and iron oxides, which occur as particles of varying sizes (<500 μm) and exhibit highly complex chemistry, as revealed by SEM-EDS. These particles are often characterised by high P–Si–Fe–Ca values, indicating areas with the association of Fe_2O_3 , SiO_2 , and $\text{Ca}_9\text{Mg}(\text{PO}_4)_7$ in discrete crystalline domains. The PBPs and accretion P–Ca–Fe rims were detected mainly in SSA_2; here, P and the other structures are in a really poor crystalline domain. This evidence is directly correlated with the higher fraction of X-ray amorphous P (especially in SSA_2), as confirmed by ICP-OES and QPA analyses.

The strong association of phosphorus with silicon and iron within the same particles, typically in the size range of 20–100 μm , significantly limits the efficiency of conventional leaching approaches aimed at phosphorus extraction. As discussed in the previous chapter, acid

treatments revealed that, depending on the nature of the SSA, phosphorus extraction efficiencies range between approximately 1% and 52%. This clearly demonstrates that such approaches are inherently limited when applied as standalone strategies, leaving, even under the most favourable conditions, a substantial fraction of phosphorus immobilized within the ash matrix.

Moreover, the intrinsic complexity of municipal mono-incinerated SSA, characterised by strong elemental associations, the presence of impurities, and elevated concentrations of heavy metals, further constrains its direct use in agricultural applications when treated through conventional or low-impact processing routes

3.4 Results and Discussion of MW thermal-treated Sewage Sludge Ashes

3.4.1 Results of Microwave Thermochemical Treatment

The MW treatment was performed using a microwave-assisted heating system consisting of SiC susceptor rings positioned inside a mullite reaction chamber placed within the microwave cavity. The SiC rings act as microwave absorbers, converting microwave radiation into thermal energy, which is subsequently transferred to the internal volume of the mullite chamber, whereas the mullite itself is substantially transparent to microwave radiation. Part of the microwave radiation may also penetrate through the SiC susceptor and interact directly with the sample, although no significant direct microwave effect was observed under the investigated conditions [119]. The temperature was monitored on the external surface of the SiC ring by means of an infrared thermometer. A schematic representation of the experimental setup is reported in Figure 24. Table 10 reports the average power values during the isothermal stage of the treatments, together with the corresponding weight losses measured after treatments at 800 °C and 1000 °C.

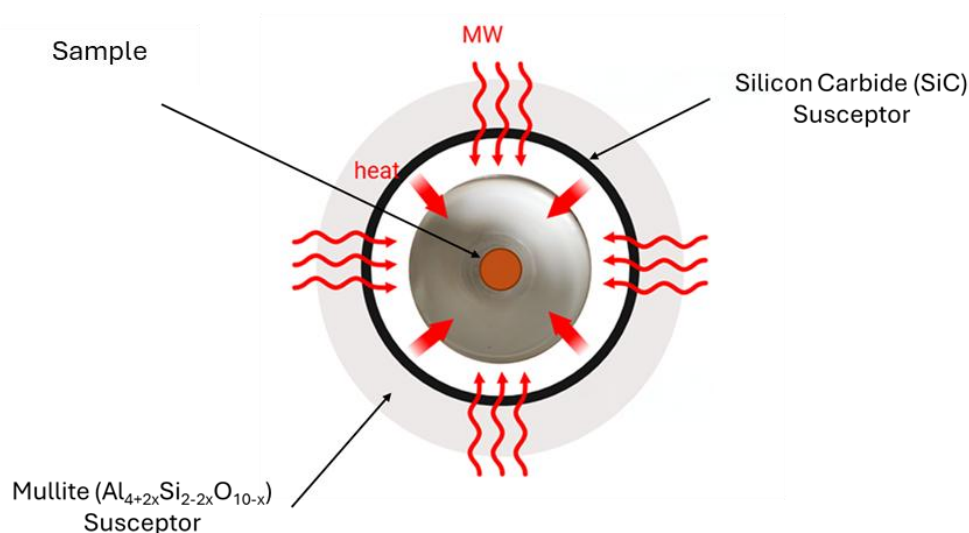


Figure 24. Schematic representation of the PYRO microwave treatment chamber. Microwave radiation penetrates the mullite chamber, being mostly absorbed by the silicon carbide (SiC) susceptor ring, which converts electromagnetic energy into heat. The generated heat is transferred to the inside area of the susceptor and subsequently to the SSA pellet positioned on a ceramic sample holder at the center of the reactor. While the SiC ring serves as the primary microwave absorber, the mullite chamber is largely transparent to microwave radiation, thereby promoting indirect heating of the sample via thermal transfer from the susceptor.

Table 10. Mean values of weight loss for SSA_1 and SSA_2 following the MW-treatment according to the reagents and the mean power of the isotherm for the two investigated temperatures.

Sample mass loss according to the Temperature					
Temperature	SSA_1		SSA_2		Mean Power
°C	wt%				W
	<i>NaHCO₃</i>	<i>KHCO₃</i>	<i>NaHCO₃</i>	<i>KHCO₃</i>	
800	23.1	20.2	25.5	22.1	410
1000	24.0	21.5	26.1	23.0	540

The weight loss is similar but slightly different for the two samples treated with the same reagent, is always higher for SSA_2, displaying a higher volatile content, especially in the CO₂ form; QPA reveals a CaCO₃ content exceeding 12 wt% in SSA_2. The treatment with NaHCO₃ consistently leads to a higher weight loss than KHCO₃, about 2.5-3% across all treatments. As will be explained in the next section, this is related to KHCO₃ lower capacity to act as a melting agent, which helps melt and recrystallize the structures of the ashes.

Microwave heating at 410-540 W can offer an energy-efficient and sustainable route where microwaves deposit energy directly into the sample or a susceptor (e.g., SiC or graphite), as in this case, enabling rapid and localized heating. The investigated temperatures (800–1000 °C) can be achieved with lower energy consumption and a short residence time, making MW treatment a promising option for sustainable thermal treatment.

3.4.2 X-ray Powder Diffraction and Scanning Electron Microscopy Results of NaHCO₃ MW-treated Sewage Sludge Ashes

X-ray QPA on the NaHCO₃ MW-treated SSAs (MW-SSA) is reported in Table 12 while the Rietveld refinement plots are reported in Figures 24, 25, 26, and 27.

The quantitative phase analysis (QPA) of the NaHCO₃ microwave-treated sewage sludge ashes (MW-SSA) is reported in Table 11, while the corresponding Rietveld refinement plots are shown in Figures 25–28. The QPA results also reveal a significant modification in the crystallinity of the samples. Regarding the phosphate phases, none of the crystalline phosphates identified in the untreated samples (whitlockite, hydroxyapatite, and tetrapotassium pyrophosphate) were detected after treatment. Instead, phosphorus appears to have recrystallized predominantly into a single crystalline phase, buchwaldite (NaCaPO₄), which

represents the main phosphate mineral in the treated ashes. Buchwaldite was detected at relatively high concentrations in all samples (24.4 – 27.6 wt%), with higher abundance observed in those treated at lower temperatures (800 °C). Phosphorus was also found in minor accessory crystalline phases, such as silicocarnotite ($\text{Ca}_5(\text{PO}_4)_2(\text{SiO}_4)$, < 0.6 wt%), and, only in the MW-SSA_2 sample treated at 1000 °C, rodolicoite (FePO_4 , 0.3 wt%). The crystalline P content for the samples treated under MW conditions significantly increased (Table 12), with values ranging from approximately 4.85 wt% (SSA_2 treated at 1000 °C) to 5.44 wt% (SSA_1 treated at 800 °C). The value of the crystalline P from the Rietveld refinement indicates that phosphorus is capable of recrystallizing in a non-amorphous, X-ray-detectable form, thus forming distinct and identifiable crystalline phases (notably buchwaldite). This highlights that not only whitlockite but also other phases, such as hydroxyapatite and potassium pyrophosphate, as well as the entire amorphous component containing phosphorus, are capable of forming new crystalline phases.

Furthermore, only a few crystalline phases of the as-collected ashes were detected in the MW-treated ones: hematite, which remains in relatively high concentrations (6.2 – 9.5 wt%), quartz, almost completely consumed during the reaction and detected in minor amounts (< 3.1 wt%), and albite ($\text{Na}(\text{AlSi}_3\text{O}_8)$). Quartz, which represents the main source of silicon within the reaction system, is progressively consumed during the thermal treatment, favouring the formation of high-temperature silicate phases. These include belite (Ca_2SiO_4), bredigite ($\text{Ca}_7\text{MgSiO}_7$), and a solid solution between akermanite ($\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$) and gehlenite ($\text{Ca}_2\text{Al}(\text{AlSiO}_7)$). The crystallisation of these silicates indicates a strong interaction between Si, Ca, and Mg within the reactive matrix, consistent with the partial melting observed during treatment. From a quantitative standpoint, their combined formation is significant, accounting for approximately 9–17 wt% of the crystalline fraction in the treated samples.

The analyses indicate a tendency for iron to crystallize predominantly as hematite and magnetite (Fe_3O_4), but also to form additional structures through associations with Ca and Si in hedenbergite ($\text{CaFe}(\text{Si}_2\text{O}_6)$) and with S in mackinawite (FeS), both of which are abundant in the ashes. Another interesting behaviour is observed for sulfur: in the untreated sample, it occurs mainly as anhydrite, whereas in the MW-treated samples, it is predominantly present as sodium sulfate polymorphs, namely thenardite and metathenardite (Na_2SO_4). These phases share the same chemical composition but differ in their crystal structure and stability conditions. According to the literature, thenardite is the stable anhydrous sodium sulfate phase under ambient conditions, while metathenardite is generally considered a high-temperature

polymorph formed during thermal treatment and subsequently retained after cooling [120] [121] .

The predominant occurrence of thenardite (2.5–9.4 wt%), the stable low-temperature polymorph of Na_2SO_4 , suggests that the initially formed high-temperature metathenardite partially transformed into thenardite during cooling.

Other crystalline phases identified are typical of the thermal treatment of this matrix with the sodium additive, including nepheline ($\text{Na}_3\text{K}(\text{Al}_4\text{Si}_4\text{O}_{16})$), lazurite ($\text{Na}_3\text{Ca}(\text{Al}_3\text{Si}_3\text{O}_{12})\text{S}$), both of which have been previously reported in similar systems, and titanite ($\text{CaTi}(\text{SiO}_4)\text{O}$) in low percentage at 1000 °C only.

Finally, all samples exhibit a considerable amorphous fraction, ranging from approximately 31.4 wt% (MW_SSA_1_800) to 34.3 wt% (MW_SSA_2_800), with no clear trend indicating a preferential formation of amorphous phases as a function of treatment temperature.

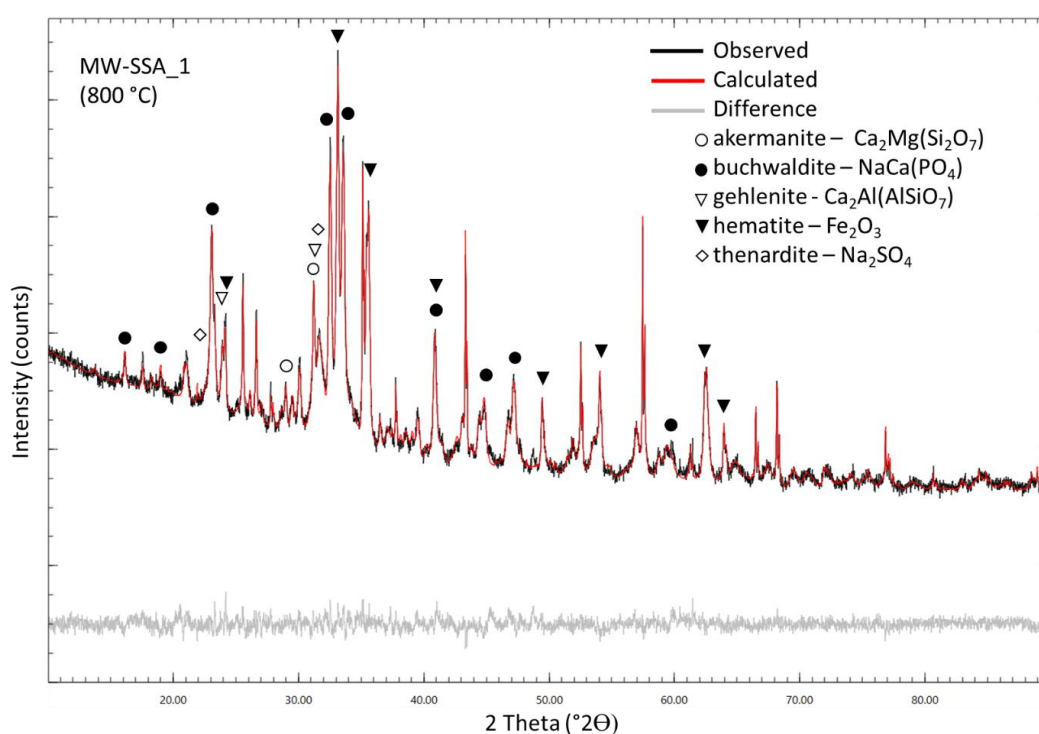


Figure 25. Rietveld refinement plot of MW-SSA_1 at 800 °C.

Table 11. QPA of the MW-treated ashes with NaHCO₃ and total crystalline P. R_{wp} is the refinement agreement factor; χ^2 is the goodness-of-fit statistic from the Rietveld refinement.

Sample		MW_SSA_1		MW_SSA_2	
Temperature (°C)		800	1000	800	1000
Cr. Phase					
name	Chemical formula				
akermanite	$Ca_2Mg(Si_2O_7)$	3.8 (2)	8.1 (2)	5.0 (2)	6.6 (2)
albite	$Na(AlSi_3O_8)$	1.0 (1)	2.7 (1)	1.0 (1)	2.1 (1)
belite	Ca_2SiO_4	2.7 (2)	1.0 (1)	2.6 (2)	1.4 (2)
bredigite	$Ca_7Mg(SiO_4)_4$	0.8 (2)	2.5 (2)	2.8 (2)	0.3 (1)
buchwaldite	$NaCa(PO_4)$	27.6 (3)	24.4 (3)	26.4 (4)	24.8 (3)
gehlenite	$Ca_2Al(AlSiO_7)$	1.8 (3)	5.9 (4)	1.5 (2)	2.7 (3)
hedenbergite	$CaFeSi_2O_6$	trace	1.1 (1)	trace	1.6 (1)
hematite	Fe_2O_3	8.8 (1)	9.3 (1)	6.2(1)	9.5 (1)
lazurite	$Na_3Ca(Al_3Si_3O_{12})S$	1.1 (1)	2.4 (1)	1.3 (2)	1.7 (1)
mackinawite	FeS	0.3 (1)	0.3 (1)	0.2 (1)	0.3 (1)
magnetite	Fe_3O_4	3.7 (1)	1.3 (1)	4.6 (1)	1.7 (1)
metathenardite	Na_2SO_4	0.8 (1)	2.0 (2)	0.4 (1)	0.2 (1)
nepheline	$Na_3K(Al_4Si_4O_{16})$	3.4 (1)	2.1 (2)	3.7 (1)	2.9 (2)
quartz	SiO_2	3.1 (1)	0.5 (1)	2.4 (2)	0.5 (1)
rodolicoite	$Fe(PO_4)$	-	trace	-	0.3 (1)
silicocarnotite	$Ca_5(PO_4)_2SiO_4$	0.3 (1)	0.5 (1)	0.6 (1)	0.5 (1)
thenardite	Na_2SO_4	9.4 (4)	2.5 (2)	7.0 (5)	8.7 (3)
titanite	$CaTi(SiO_4)O$	-	0.3 (1)	-	0.8 (1)
amorphous		31.4 (9)	33.1 (8)	34.3 (9)	33.4 (8)
Cr. Phosphorus	P	5.44	4.85	5.25	5.00
R_{wp}		2.05	2.15	2.01	1.99
χ^2		1.87	2.00	1.80	1.76

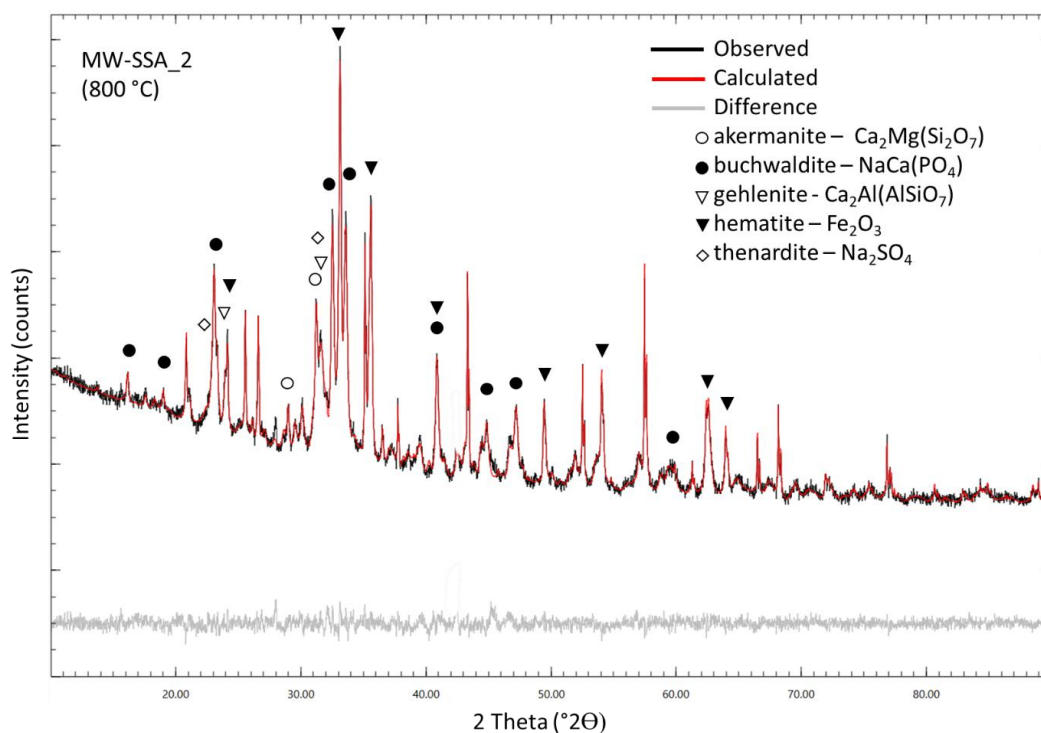


Figure 26. Rietveld refinement plot of MW-SSA_2 at 800 °C.

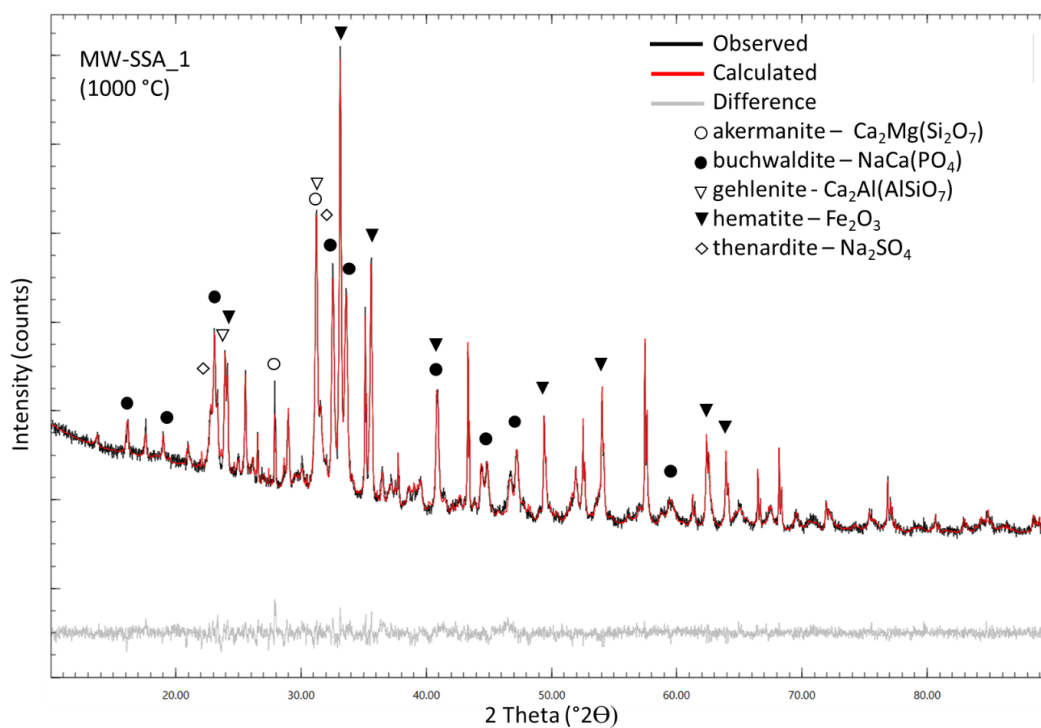


Figure 27. Rietveld refinement plot of MW-SSA_1 at 1000 °C.

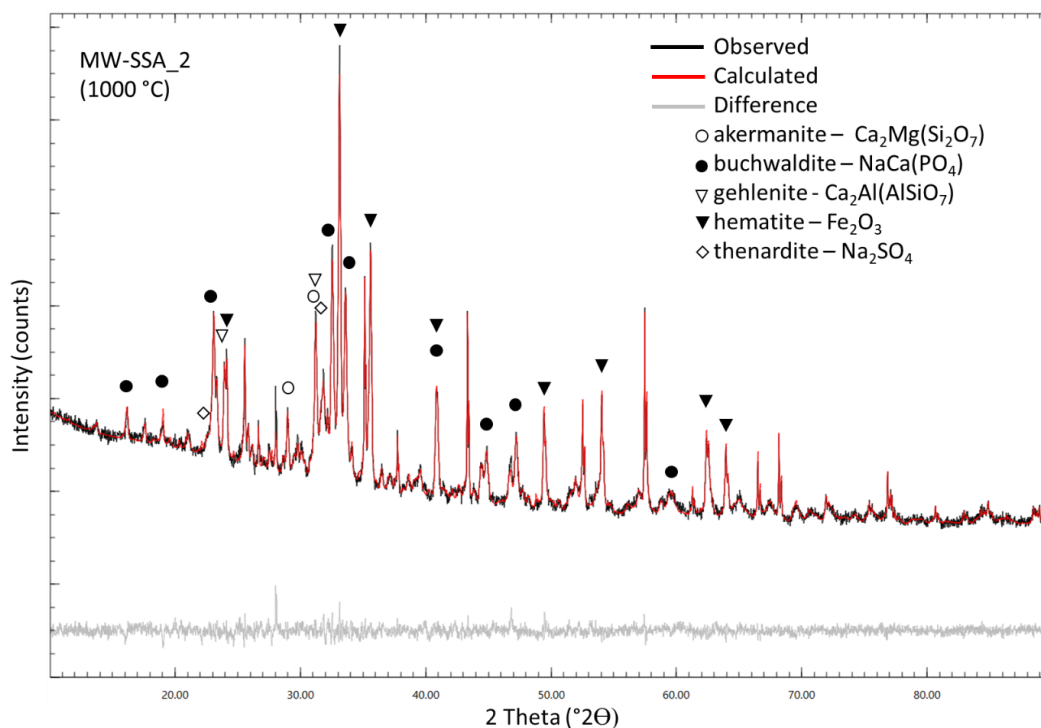


Figure 28. Rietveld refinement plot of MW-SSA_2 at 1000 °C.

Figures 29 and 30 present the SEM-EDS images and Table 13 the semi-quantitative EDS of the samples treated at 800 and 1000 °C in NaHCO_3 , respectively, highlighting the microstructural and compositional differences induced by the MW-treatment. These data were extremely useful for establishing a direct correspondence with the phases identified by QPA and for understanding the overall evolution of the reaction. As shown in Figures 29A and 30A, which represent the vertical cross-section of the SSA_1 tablet treated at 800 and 1000 °C, respectively, it is evident that the thermal treatment involved a transient fluid phase, which completely modified the original crystalline framework of the ash. The structures previously observed are almost unrecognizable, particularly in the sample treated at 1000 °C (Figure 30). At 800 °C, however, both the upper and lower edges of the pellet display a microstructure that still partially resembles the original morphology (Figure 29A). P–Si–Fe spheres are still visible, although their internal structure appears significantly altered (Figure 29F). In Figures 29B and 30B, which show magnified views of the vertical cross-sections, a bubble-like pattern is clearly visible, consisting of phosphates blebs embedded in a grey background matrix interspersed with elongated white crystalline areas without a continuous texture. Figures 29C and 30C–D present further magnifications, where four distinct phases can be recognized. The light- and dark-grey groundmass, with a chemistry dominated by Si–Al–Mg–Ca (spectra Z1 and Z2, Figure 29C and spectra Z1 and Z2, Figure 30C), reflects the presence of the high-temperature silicate crystalline

phases akermanite–gehlenite solid solution, belite, and bredigite. Phosphate blebs, enriched in P–Ca–Na (spectrum Z3 Figure 29C-D and spectrum Z3 Figure 30D), are dispersed throughout the Si-rich matrix and also observed within the pellet pores (Figure 29E-D). These blebs, based on their chemical composition and predominant distribution in the sample, correspond to the NaCa(PO₄) phase identified in high amounts through XRD analysis. Finally, iron oxide crystals (spectrum Z4, Figure 29C and spectrum Z4, Figure 29D), hematite, and magnetite are present, occasionally displaying a circular distribution pattern of the original P–Si–Fe spheres (Figures 29F and 30C).

Table 12. EDS semi-quantitative elemental analysis of MW-SSA_1 at 800 °C and 1000 °C, reacted with NaHCO₃.

Sample	800 °C				1000°C			
	Z1	Z2	Z3	Z4	Z1	Z2	Z3	Z4
Element								
O	34.2	36.0	37.2	22.5	32.4	32.9	39.1	18.3
P	0.5	0.6	21.9		0.4	0.9	13.7	
Ca	24.8	9.1	27.3	0.6	26.8	6.1	24.5	1.3
Na	3.5	7.8	10.0		3.4	6.9	9.1	0.6
Mg	3.2	1.6		1.7	3.5	0.9	0.6	0.7
K		2.4				3.2	0.6	
S		0.5					0.9	
Al	0.9	1.4			2.6	4.5	1.0	0.5
Si	22.3	27.4	2.3		22.5	25.7	7.2	1.3
Fe	10.3	12.6	1.3	70.9	8.5	17.8	3.4	75.8
Ti		0.7		4.4		1.1		1.6
Cl	0.4							

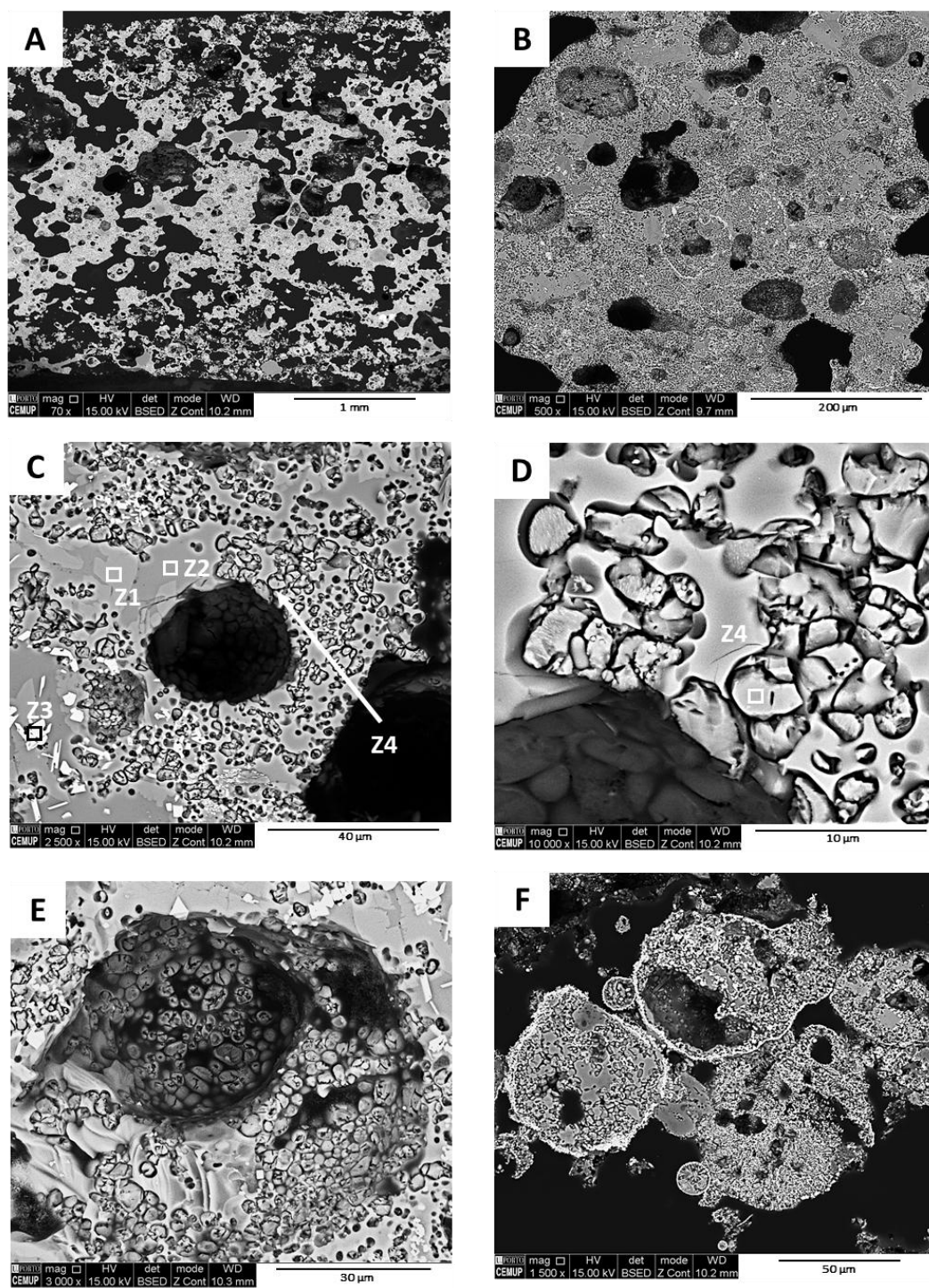


Figure 29. SEM-EDS analyses of MW-treated SSA with NaHCO_3 at 800 °C: (A) low magnification of MW-SSA (sample SSA_1; BSE mode; 70 $\times$); (B) higher magnification of MW-SSA (sample SSA_1; BSE mode; 500 $\times$); (C) High magnification of MW-SSA where the new structures are clearly visible and spectra Z1, Z2, Z3, Z4 (sample SSA_1; BSE mode; 2500 $\times$); (D) High magnification of the NaCaPO_4 blebs (sample SSA_1; BSE mode; 10000 $\times$); (E) high magnification of the internal structure of sample hole, displacing the NaCaPO_4 blebs (sample SSA_2; BSE mode; 3000 $\times$); (F) structure of the P-Si-Fe

displacing NaCaPO_4 blebs in the and Fe mostly migrate to the spheres surface (sample SSA_2; BSE mode; 1500 $\times$).

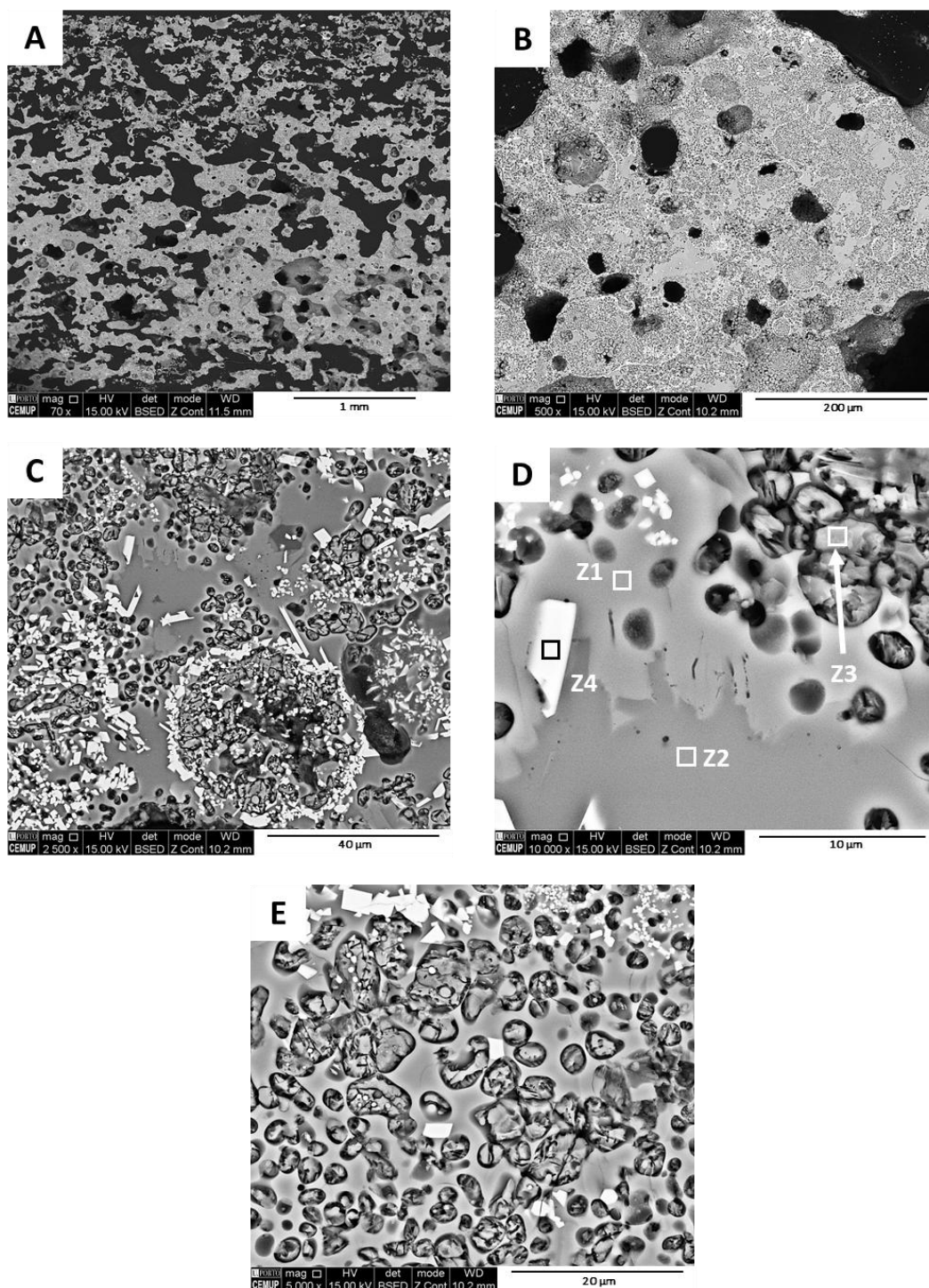


Figure 30. SEM-EDS analyses of MW-treated SSA with NaHCO_3 at 1000 °C: (A) low magnification of MW-SSA (sample SSA_2; BSE mode; 70 $\times$); (B) higher magnification of MW-SSA (sample SSA_2; BSE mode; 500 $\times$); (C) high magnification of MW-SSA where the new structures are clearly visible and the P-Si-Fe sphere almost completely collapsed (sample SSA_2; BSE mode; 2500 $\times$); (D) NaCaPO_4 blebs, Fe oxides and silica matrix, spectra Z3, Z4, Z1 and Z2 (sample SSA_1; BSE mode; 10000 $\times$); (E)

magnification of the new structures and the NaCaPO₄ well defined edges (sample SSA_1; BSE mode; 5000×).

The XRPD data highlight that treatment with NaHCO₃, both at 800 °C and 1000 °C, produces a highly synthesized product in which the crystalline structures are completely modified. Phosphorus is predominantly crystallized in the buchwaldite phase, which exhibits high bioavailability [122] [112] [32] and to a lesser extent in insoluble forms such as silicocarnotite and rodolicoite (SSA_2 at 1000 °C). The blebs are clearly visible in the SEM images, having a size wider than 10 µm; the other phosphates were not identified by this technique; they are likely located in Si–Ca–P interfacial zones with a lower degree of synthesis, possibly corresponding to the upper and lower portions of the pellet. This assumption is supported by the observation that silicocarnotite is found in higher concentrations in samples treated at lower temperatures (800 °C).

Finally, it can be stated that the post-treatment structure exhibits well-defined zones of buchwaldite crystals, distinctly separated from the homogeneous silica-based matrix, along with hematite and magnetite crystals that appear to be disconnected from the system. The major elements P, Si, and Fe, which were initially bound together in poorly defined structures, are now segregated into distinct components within an overall highly complex matrix. Sodium, originating from sodium bicarbonate, shows a preferential association with phosphorus within the buchwaldite blebs and subsequently with sulfur to form thenardite and finally with silicon in nepheline and lazurite crystalline structure.

3.4.3 X-ray Powder Diffraction and Scanning Electron Microscopy Results of KHCO₃ MW-treated Sewage Sludge Ashes

In this section, the XRD analyses are qualitative only, as the crystalline structure of KCaPO₄ formed during the treatment has not yet been fully resolved. Consequently, no crystallographic information file (CIF) or reliable structural model is currently available for this phase. Since Rietveld refinement requires accurate crystallographic data, including lattice parameters, atomic positions, and symmetry information, quantitative phase analysis of KCaPO₄ could not be reliably performed. Table 13 reports the crystalline phases identified in the treated samples. The samples treated at 800 and 1000 °C display comparable degrees of crystallinity with respect to the crystalline phases identified. Under these conditions, the formation of KCaPO₄ is observed, as with previous NaHCO₃-assisted treatment, which yielded a markedly higher

abundance of buchwaldite. Hydroxyapatite and whitlockite are also detected and appear to have partially retained their structural integrity following thermal exposure, particularly in the case of hydroxyapatite. Silicocarnotite is also present but only for the SSAs treated at 800 °C. Moreover, several sulfate phases were identified, including arcanite (K_2SO_4), apththitalite ($\text{K}_3\text{Na}(\text{SO}_4)_2$, detected exclusively at 1000 °C), and langbeinite ($\text{K}_2\text{Ca}_2(\text{SO}_4)_3$). Among the other detected phases, silicates such as residual quartz and newly formed leucite (KAlSi_2O_6) were identified, along with iron oxides including haematite and magnetite. Figures 31 and 32 show the diffraction patterns of the SSA_1 sample treated at 800 °C and 1000 °C, respectively. Although it is difficult to quantitatively assess the relative abundance of each phase, the diffraction peaks corresponding to quartz, hydroxyapatite, and whitlockite are more intense in the sample treated at 800 °C, whereas those of KCaPO_4 , langbeinite, and arcanite exhibit higher intensities at 1000 °C. This trend suggests a milder degree of solid-state reaction at 800 °C and a more extensive synthesis process at 1000 °C.

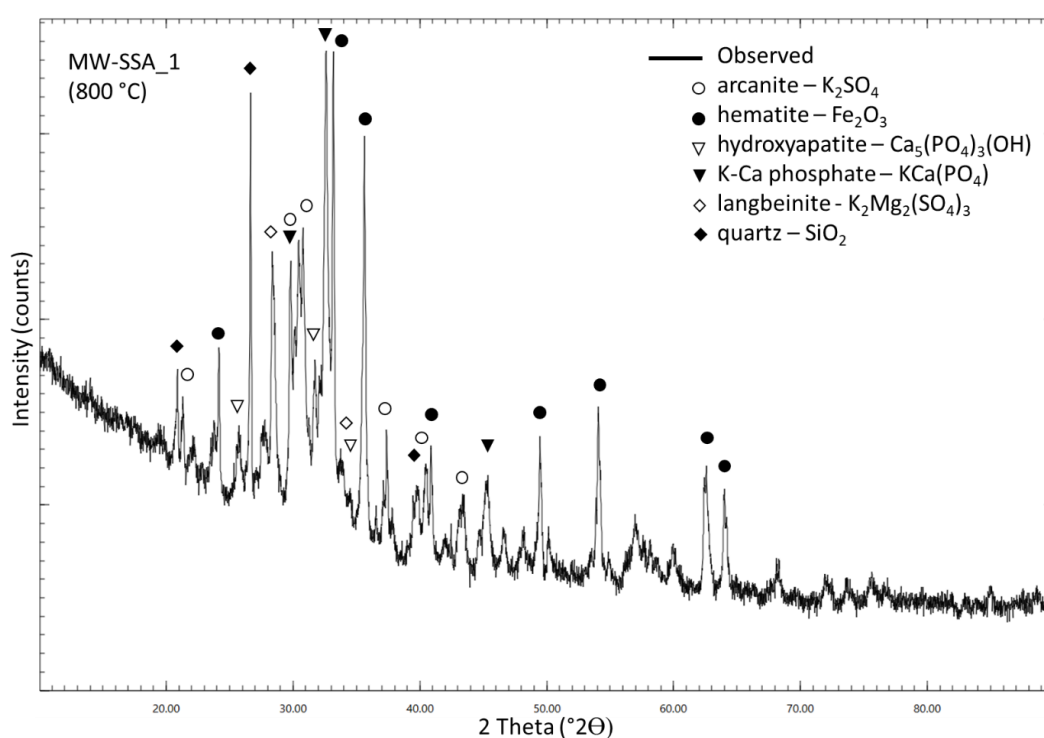


Figure 31. Diffraction pattern of MW-SSA_1 (800 °C) and qualitative phase analysis.

Table 13. Qualitative phase analysis of SSA_1 and SSA_2 treated with KHCO_3 at 800 °C and 1000 °C.

Sample		MW_SSA_1		MW_SSA_2	
Temperature (°C)		800	1000	800	1000
Cr. Phase					
name	Chemical formula				
akermanite	$\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$	x	x	x	x
albite	$\text{Na}(\text{AlSi}_3\text{O}_8)$	x	-	x	-
arcanite	K_2SO_4	x	x	x	x
aphthitalite	$\text{K}_3\text{Na}(\text{SO}_4)_2$	-	x	-	x
gehlenite		-	x	-	x
hematite	Fe_2O_3	x	x	x	x
hydroxyapatite	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	x	x	x	x
K-Ca phosphate	KCaPO_4	x	x	x	x
langbeinite	$\text{K}_2\text{Ca}_2(\text{SO}_4)_3$	x	x	x	x
leucite	$\text{K}(\text{AlSi}_2\text{O}_6)$	x	x	x	x
magnetite	Fe_3O_4	x	x	x	x
quartz	SiO_2	x	x	x	x
silicocarnotite	$\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$	x	-	x	-
whitlockite	$\text{Ca}_9\text{Mg}(\text{PO}_4)_7$	x	x	x	x

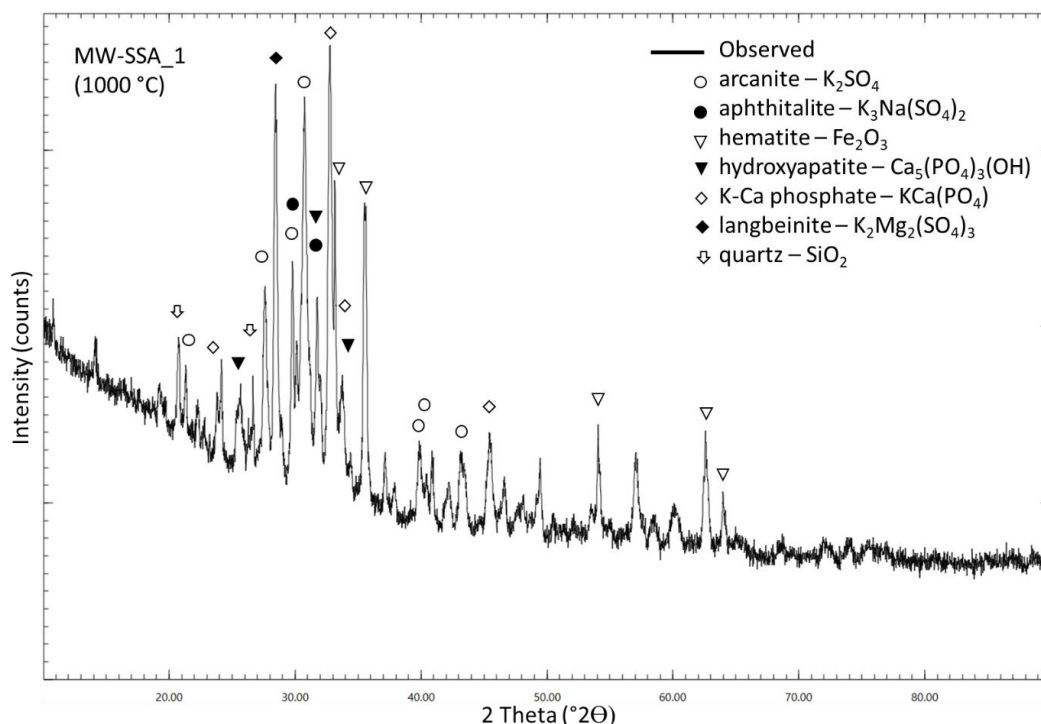


Figure 32. Diffraction pattern of MW-SSA_1 (1000 °C) and qualitative phase analysis.

Figures 33 and 34 show the SEM micrographs of the SSA_1 sample treated at 800 °C and 1000 °C, respectively, together with the corresponding EDS analysis areas, whose spectra are reported in Table 14.

In agreement with the XRPD results, the SEM-EDS analyses indicate a limited degree of solid-state reaction for the sample treated at 800 °C (Figure 33A), where many of the pre-existing morphological features are still recognisable. In Figure 33B, which shows a magnified view of the central area of the previous image, rounded P–Si–Fe spheres and relatively large quartz clasts (spectrum Z1) can be observed, partially interconnected by local melting zones where adjacent particles appear fused together. Figure 33C provides a further magnification, revealing the presence of small, poorly defined P-rich domains resembling phosphatic blebs, although significantly smaller and less distinct than those observed in other treatments. The highest magnification (Figure 33D) confirms the presence of submicrometric bleb-like structures composed primarily of K–Ca–P (spectrum Z3), occurring adjacent to regions where all the major elements (Ca, P, Si, K, Fe) coexist (spectrum Z2). Overall, these observations suggest that the reaction proceeded only partially, forming $KCaPO_4$ in localised zones rather than homogeneously throughout the material, indicating an incomplete or spatially constrained synthesis process at 800 °C.

In contrast, the specimens treated at 1000 °C exhibit a markedly different microstructural arrangement. The vertical cross-section of the pellet (Figure 34A) closely resembles that of the Na-treated sample (Figure 29A), except for the upper border region, where the degree of synthesis appears slightly lower. In Figure 34B, showing a magnified view of the same area, a grey groundmass can be observed, containing dispersed bleb-like features and irregularly distributed white crystalline aggregates. Figures 34C (spectrum Z3) and 34D provide a clearer view of these blebs, which are embedded within a heterogeneous matrix characterised by light-grey (Z1) and dark-grey (Z3) zones. These regions display a chemically complex composition in which all major elements—Ca, P, Si, K, and Fe—remain intimately intermixed at relatively high concentrations, indicating that phase separation is still incomplete at this temperature. Finally, bright crystalline domains enriched in Fe and O were observed (spectrum Z4), corresponding to the formation of iron oxide phases, namely hematite and magnetite, containing also some Ti and manganese (Mn). A higher magnification provides further insight into the progression of the reaction. Figure 34F shows an area where iron oxide crystals (appearing as bright white domains) are clearly visible. These regions exhibit poorly developed structures with indistinct boundaries and a complex chemical composition: spectrum Z5 corresponds to a Si–K-rich area, Z6 to a Ca–P-rich domain, Z7 to a Ca–K-enriched zone, and Z8 to a P–Ca–K-rich region. The latter, both in morphology and composition, appears to represent a phosphatic bleb in the early stage of formation.

Table 14. EDS semi-quantitative elemental analysis of MW-SSA_1 at 800 °C and 1000 °C, reacted with $KaHCO_3$

Sample	800 °C			1000°C							
	Z1	Z2	Z3	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8
Element	wt %										
O	44.6	35.0	33.1	32.1	29.7	24.9	22.8	28.7	31.6	29.5	29.1
P	-	5.1	14.7	14.3	-	18.2	-	0.9	16.3	1.4	18.4
Ca	-	12.7	17.3	34.9	25.0	32.4	0.5	2.9	39.9	12.1	38.0
Na	-	0.3	0.3	-	-	0.9	0.9	-	-	-	-
Mg	-	0.9	0.4	0.3	0.4	-	8.9	0.5	-	1.2	-
K	-	19.4	21.0	4.7	0.8	20.8	0.7	23.9	4.9	17.9	8.6
S	-	-	-	-	-	-	-	-	-	-	1.0
Al	-	3.1	1.3	0.3	0.3	-	0.2	6.8	-	0.6	-
Si	55.4	15.5	6.8	6.8	14.3	2.8	1.4	18.3	4.4	18.4	3.3
Fe	-	4.2	4.1	6.0	23.6	-	62.8	18.1	3.0	15.3	1.6
Ti	-	3.8	1.0	0.7	5.8	-	0.6	-	-	3.6	-
Cl	-	-	-	-	-	-	-	-	-	-	-
Mn	-	-	-	-	-	-	1.3	-	-	-	-

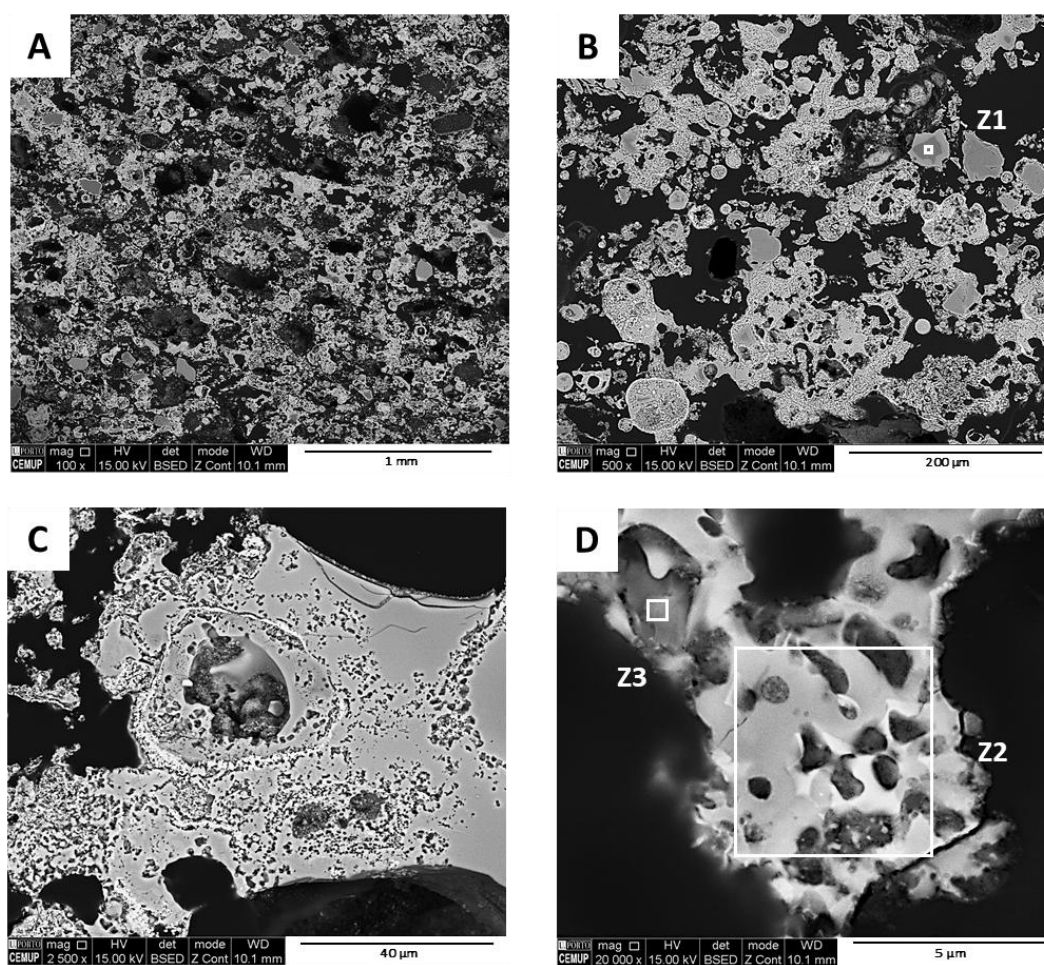


Figure 33. SEM-EDS analyses of MW-treated SSA with KHCO_3 at 800°C : (A) low magnification of MW-SSA reflecting almost the same structures as before the treatment (sample SSA_1; BSE mode; 70 $\times$); (B) higher magnification of MW-SSA, quartz grain are still visible in spectra Z1 (sample SSA_1; BSE mode; 500 $\times$); (C) High magnification of MW-SSA here structures resembling blebs can be observed, likely corresponding to KCaPO_4 blebs in formation (sample SSA_1; BSE mode; 2500 $\times$); (D) High magnification of the very small sized KCaPO_4 blebs and spectra Z2-Z3 (sample SSA_1; BSE mode; 20000 $\times$).

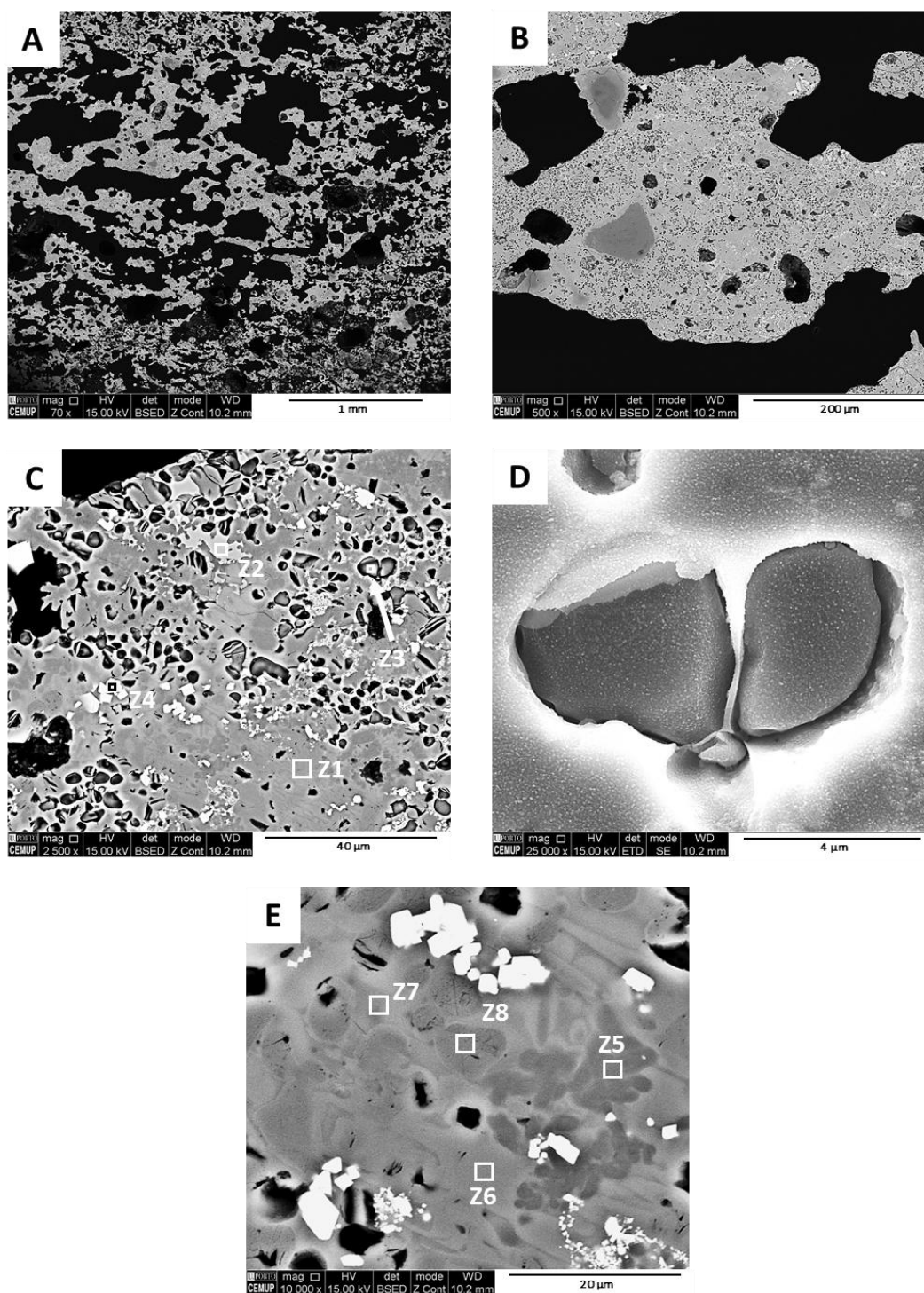


Figure 34. SEM-EDS analyses of MW-treated SSA with KHCO_3 at 1000 °C: (A) low magnification of MW-SSA where the a new framework is visible (sample SSA_2; BSE mode; 70×); (B) higher magnification of MW-SSA resembling the NaHCO_3 structures after the treatment(sample SSA_2; BSE mode; 500×); (C) High magnification of MW-SSA where the new structures are clearly visible and spectra Z1, Z2, Z3, Z4 (sample SSA_2; BSE mode; 2500×); (D) High magnification of the KCaPO_4 blebs (sample SSA_1; SE mode; 25000×); (E) region characterised by the presence of KCaPO_4 blebs

with diffuse boundaries, indicative of an early stage of formation, embedded within a silica-rich matrix (sample SSA_2; BSE mode; 10000×).

In conclusion, the treatment at 800 °C resulted in limited formation of $\text{KCa}(\text{PO}_4)$ blebs and a generally low degree of synthesis, which appears to have occurred predominantly in the solid state, with only minor localised partial melting of certain regions within the pellet. In contrast, the sample treated at 1000 °C exhibits a microstructure indicative of a higher degree of reaction, with clearly developed K–Ca phosphatic blebs. However, the persistence of whitlockite and hydroxyapatite, particularly in the 800 °C specimen, suggests that KHCO_3 could not promote a complete conversion of phosphorus into newly formed potassium-calcium phosphate phases. This behaviour may be related to the high thermal stability of the original phosphate phases, combined with incomplete solid-state reaction kinetics under the investigated conditions. In addition, the larger ionic radius of K^+ compared to Na^+ may reduce diffusion efficiency and limit the extent of phase transformation during treatment. The results, therefore, suggest that the selected treatment conditions were insufficient to achieve a complete redistribution of phosphorus into newly formed K-bearing crystalline phases. As evidenced by the SEM-EDS images, phosphorus remains partly associated with Si and Fe, which significantly restricts its solubility and, consequently, its potential bioavailability.

3.4.4 Feasibility of the Saline Additive Used to Transform Phosphorus and Phosphates

Under identical stoichiometric conditions, corresponding to equal Na and K contents in the 70 wt% SSA–30 wt% salt formulations, the two bicarbonate additives exhibited distinct thermochemical behaviours during heat treatment. Sodium bicarbonate (NaHCO_3) proved to be a more effective melting agent, being capable of significantly lowering the local melting point and thereby promoting an extensive degree of fluid-state reaction even at the lower treatment temperature. In contrast, potassium bicarbonate (KHCO_3) did not exhibit the same fluxing efficiency; it appears to decompose and induce only localised melting phenomena, in which partial fusion between adjacent grains occurs. This behaviour is particularly evident at 800 °C. A clear indicator of this difference is the presence of quartz, which is almost eliminated after treatment with NaHCO_3 (especially at 1000 °C), while it remains one of the dominant crystalline phases in samples treated with KHCO_3 , particularly at 800 °C.

From a chemical standpoint, NaHCO_3 is markedly more efficient in promoting the transformation of phosphorus-bearing phases into well-defined crystalline compounds, primarily buchwaldite ($\text{NaCa}(\text{PO}_4)$). Conversely, KHCO_3 facilitates only a partial formation of

KCaPO₄, whose crystal structure has not yet been fully resolved through refinement analyses. Residual whitlockite and hydroxyapatite phases are still detected, indicating incomplete conversion of P. Furthermore, SEM–EDS analyses reveal that part of the phosphorus remains bound to Si and Fe, thereby significantly limiting its solubility.

The behaviour of the two alkali elements also differs substantially. In this complex reactive system, sodium exhibits a stronger affinity for phosphorus, later combining with sulfur to form thenardite/metathenardite (Na₂SO₄ polymorphs) and subsequently with silicon to generate nepheline (NaAlSiO₄). Potassium, on the other hand, shows a greater tendency to react with sulfur, leading predominantly to the crystallisation of arcanite (K₂SO₄) (the main sulfate phase at both treatment temperatures) before incorporating into P–Si-bearing phases of more complex structure. Overall, under the conditions adopted in this study, NaHCO₃ exhibits distinctly superior reactivity and melting capacity, achieving a more complete conversion of phosphorus into crystalline phases with well-defined chemical and structural characteristics.

3.5 Results and Discussion of the Neutral Ammonium Citrate (NAC) Leaching

This section discusses the elemental extraction, especially for P, related to the dry matter (≈ 1 g of sample) obtained after leaching in neutral ammonium citrate. These values are compared with the total elemental contents to evaluate the extraction efficiency for both the as-collected and MW-treated materials.

The extraction efficiency in NAC for the as-collected ashes is compared with the total elemental content determined by acid digestion.

Since the elemental concentrations in the thermochemically treated samples differ from those determined by acid digestion of the raw ashes, the total contents were recalculated to provide a consistent basis for comparison. It was recalculated to account for both the initial dilution introduced by mixing the SSA with the additive (approximately in a 70:30 mass ratio) and the effective mass losses measured after the thermal treatment (as reported in Table 11). These corrections were applied to ensure that the final concentrations, expressed in mg/kg, accurately reflect the composition of the solid residue after processing. The approach assumes no volatilization or elemental loss during treatment, allowing a more reliable comparison between the as-collected and treated samples, particularly in the evaluation of phosphorus retention and redistribution among the newly formed mineral phases. The following equation (9) expresses the final content of an element after dilution with the saline additive and thermal process, accompanied by a measurable mass loss of the sample:

$$E_f = E_0 * (F_D)/(F_{ML}) \quad (9)$$

Where E_f is the final elemental content after the MW-treatment, E_0 is the total content determined by digestion, F_D is the dilution factor (sample – reagent), and F_{ML} is the mass loss factor following the thermochemical treatment.

3.5.1 Leaching in Neutral Ammonium Citrate and Weight Loss

The leaching in Neutral Ammonium Citrate was performed according to the procedure explained in section 3.1.3, using ≈ 1 g of sample and 100 mL of pH 7 NAC.

Table 15 reports the mass losses following the leaching tests on the as-collected and MW-treated ashes, corresponding to the percentage of material effectively solubilised during the process. The solid residue was washed, fully dried at 105 °C, weighed, and subsequently characterised by XRPD and SEM-EDS.

The as-collected ashes total leached mass for both samples was approximately 36%. Following the thermochemical treatment, this value increased significantly (particularly for the samples treated with NaHCO_3) where the leached fraction ranged between 50 and 57%, while for KHCO_3 -treated samples it ranged between 43 and 54%. Treatments carried out at the lower temperature (800 °C) generally produced more soluble products, whereas synthesis at 1000 °C consistently resulted in materials of lower solubility. Finally, under identical conditions of reagent and temperature, sample SSA_1 exhibited higher solubility than SSA_2 after treatment with NaHCO_3 , while the opposite trend was observed for KHCO_3 -treated samples. Therefore, no linear correlation in solubility behaviour can be established between the two treatments.

Table 15. mass % loss following the NAC leaching test on the as-collected and MW-treated SSAs.

Sample	SSA_1		SSA_2	
	%			
As-collected	35.9		36.2	
Reagent	<i>NaHCO₃</i>	<i>KHCO₃</i>	<i>NaHCO₃</i>	<i>KHCO₃</i>
MW 800 °C	56.7	50.6	56.4	54.4
MW 1000 °C	54.9	43.2	50.2	47.2

3.5.2 As-collected Sewage Sludge Ashes Leachates and Solid Residues

In Table 16, the chemical analyses of the NAC-leached SSA_1 and SSA_2 solutions, as collected, are reported. The macronutrients and heavy metals concentrations are expressed in mg/kg of the total ash amount used during leaching (approximately 1 g).

*Table 16. Chemical analysis of NAC-leached SSA_1 and SSA_2. Elements marked by * collected with TXRF, analyses for Cr (VI) with UV-vis. LOQ is the Limit of Quantification reported in Table 7*

Sample	As-collected					
	SSA_1			SSA_2		
Element	mg/kg					
P	15715	±	908	11715	±	907
Na	1391	±	45	1278	±	45
K	1363	±	182	1830	±	181
Ca	86703	±	4542	88017	±	4534
Mg	3376	±	182	3174	±	181
S	16078	±	908	10056	±	907
Cd*	n.d.					
Ti*	231	±	39	306	±	31
Cr*	31	±	10	28	±	6
Cr (VI)	n.d.					
Fe*	6443	±	129	9165	±	123
Ni*	47	±	15	36	±	11
Cu*	130	±	3	133	±	3
Zn*	704	±	9	774	±	10
Pb*	41	±	13	21	±	8
As*	n.d.					

The values reported in Table 17 have limited significance on their own unless compared with the total content of the same elements. For this reason, Figures 35 and 36 present a comparison of the total elemental content with the corresponding extraction values obtained via NAC leaching. Some of the elements detected at low concentrations after digestion, such as Cd and As, were not detected.

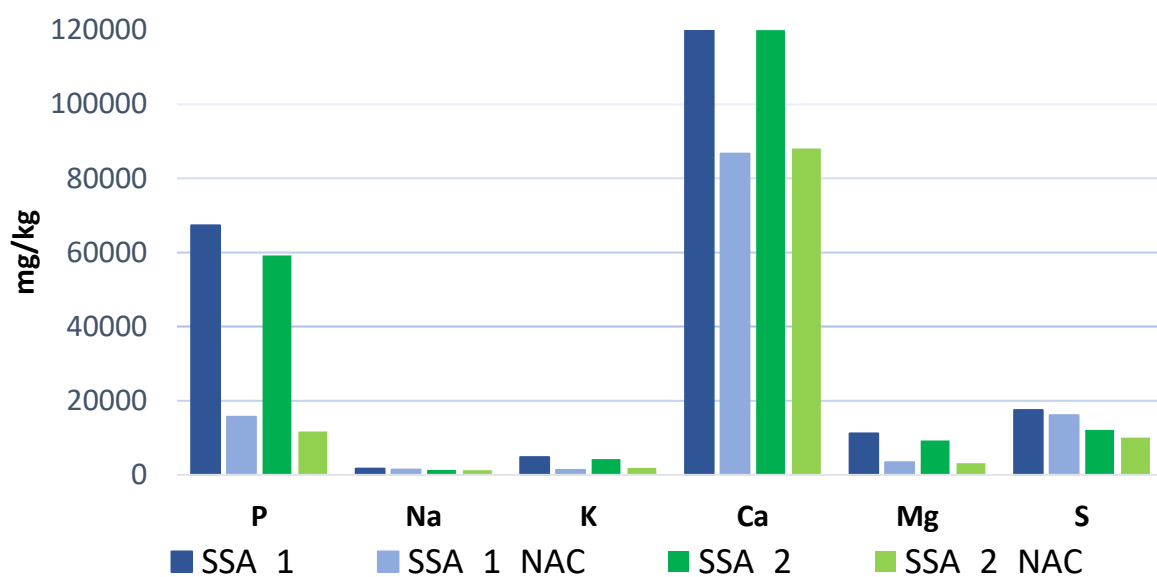


Figure 35. Comparison between the total content of macronutrients (SSA_1 and SSA_2) and their solubility in NAC (SSA_1_NAC and SSA_2_NAC) reported to the total mass leached.

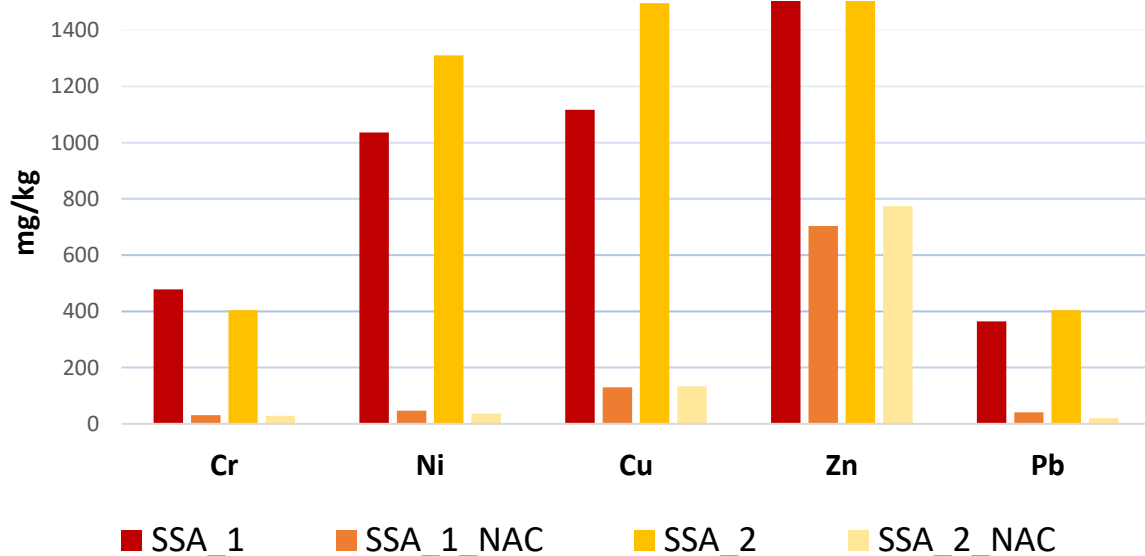


Figure 36. Comparison between the total content of heavy metals (SSA_1 and SSA_2) and their solubility in NAC (SSA_1_NAC and SSA_2_NAC) reported to the total mass leached.

For sample SSA_1, the measured P concentration is approximately 1.6%, while for SSA_2 it is around 1.2%. In the graphs shown in Figure 35, it is evident that the solubility of phosphorus (P) in NAC for the as-collected matrices is extremely low. These values correspond to low extraction efficiencies, approximately 23.3% and 19.8% of the total P for SSA_1 and SSA_2, respectively. Table 17 reports the results of the quantitative phase analysis (QPA) of the solid residues (Figures 37 and 38) after leaching, which indicate a significant presence of whitlockite,

13.9 wt% in SR_SSA_1 and 9.9 wt% in SR_SSA_2, and hydroxyapatite, with about 1.5 wt% remaining in the samples. The total content of crystalline P also remains high, approximately 3.10 wt% and 2.29 wt% for SR_SSA_1 and SR_SSA_2, respectively. Slightly lower than the as-collected ashes due to the complete dissolution of $K_4P_2O_7$.

The SEM–EDS analyses (Figure 39 and Table 18, EDS spectra) further confirm the high phosphorus content in the residues. Phosphorus is still associated at high concentrations (spectra Z2 and Z4, Table 19) with P–Si–Fe sphere structures that remain morphologically intact (Figures 39C, D, and E), with no signs of compound dissolution, although they are fragmented during milling. Furthermore, P is found in well-formed calcium phosphate crystals, including whitlockite crystals (Figure 39F).

The other elements classified as macronutrients (Ca, Mg, Na, K, S) exhibit different solubility behaviours but have the same trend for both samples. The solubility is relatively high for S (80–90%), Ca (60–70%), and Na (80–95%), and moderate for K and Mg (approximately 30–40% of the total content). The high solubility of S and Ca in NAC (Table 16 – Figures 35 and 36) is confirmed by both QPA and SEM–EDS data. Sulfur is detected in low amounts primarily due to the dissolution of anhydrite crystals, which are no longer detected in the QPA results. Calcium is also mainly dissolved in the form of calcite, detected in residues (≈ 1.3 wt%) (Table 17), but still present and bonded in all the particles analysed with SEM-EDS, as shown in Table 18.

The heavy metals classified as contaminants (Ni, Zn, Cu, Cr(VI), and Pb) exhibit generally low solubility in neutral ammonium citrate (NAC). Among them, Zn shows the highest solubility, accounting for approximately 17% of its total content, whereas the other metals display solubility values equal to or below 11%. Hexavalent chromium (Cr(VI)) was not detected, and the Cr concentrations reported therefore refer to total chromium. Table 16 reports the results for Fe and Ti, which are not classified as contaminants under current regulations. These elements also exhibit very low solubility compared to their total contents, with approximately 6–7% for Cr and less than 5% for Fe and Ti in both samples.

QPA analyses provide further insight into the solid residues. The main crystalline phases identified after leaching are quartz and hematite, together with the non-leached whitlockite. The remaining phases are essentially the same as those detected in the as-collected ashes—namely albite, cristobalite, goethite, pigeonite, portlandite, srebrodolskite, and tridymite (all present in amounts below 5 wt%). The XRD amorphous phase content remains approximately constant, at around 40 wt% for both samples. A slight increase is observed in SR_SSA_1 compared with the as-collected material, whereas SSA_2 shows a marginal decrease. These variations are

minor and likely reflect small structural rearrangements or partial dissolution of amorphous components during the leaching process, rather than any substantial transformation of the overall phase assemblage.

Table 157. QPA of the solid residue (SR) of SSA_1 and SSA_2 after the NAC leaching, and the value of total crystalline P. R_{wp} is the refinement agreement factor; χ^2 is the goodness-of-fit statistic from the Rietveld refinement.

Sample		SR_SSA_1	SR_SSA_2
Cr. Phase	Chemical formula		
albite	$Na(AlSi_3O_8)$	3.4 (2)	4.9 (2)
calcite	$CaCO_3$	1.3 (1)	1.2 (1)
cristobalite	SiO_2	1.2 (1)	2.6 (2)
goethite	$FeO(OH)$	1.0 (1)	1.4 (1)
hematite	Fe_2O_3	14.1 (2)	11.5 (2)
hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	1.2 (2)	1.4 (2)
pigeonite	$(Mg,Fe,Ca)_2Si_2O_6$	4.2 (2)	5.3 (2)
portlandite	$Ca(OH)_2$	0.4 (1)	0.8 (1)
quartz	SiO_2	16.9 (3)	17.7 (3)
srebrodolskite	$Ca_2Fe_2O_5$	0.3 (1)	1.1 (1)
tridymite	SiO_2	1.2 (1)	1.6 (1)
whitlockite	$Ca_9Mg(PO_4)_7$	13.9 (3)	9.9 (3)
Amorphous		40.9 (10)	40.6 (9)
Cr. Phosphorus	P	3.10	2.29
R_{wp}		1.85	2.05
χ^2		2.03	2.53

Additional structural details of the SR are shown in SEM-EDS Figures 39A and 39B, where, at low magnification (750 $\times$), it can be observed that the particles generally maintain a size below 100 μm , with some larger grains occasionally present (e.g., Figure 39B). Numerous quartz grains (labelled as Qz in the images) are clearly visible, while hematite remains as a coating around the P–Si–Fe spheres and is also dispersed throughout the sample.

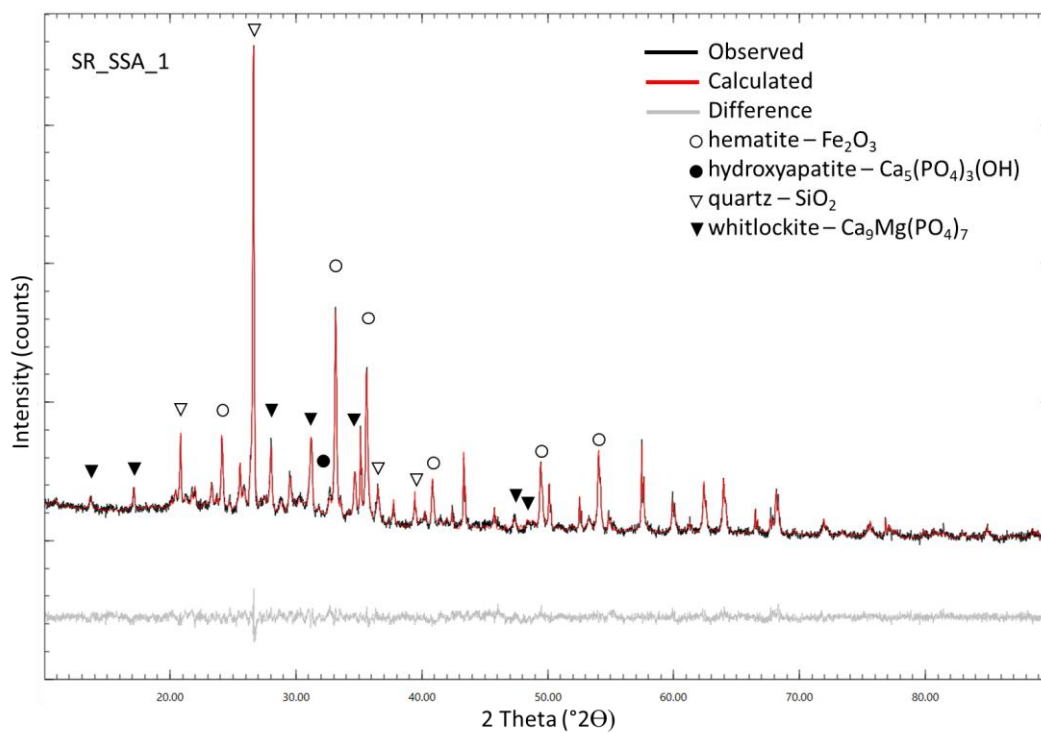


Figure 37. Rietveld refinement plot of SR_SSA_1

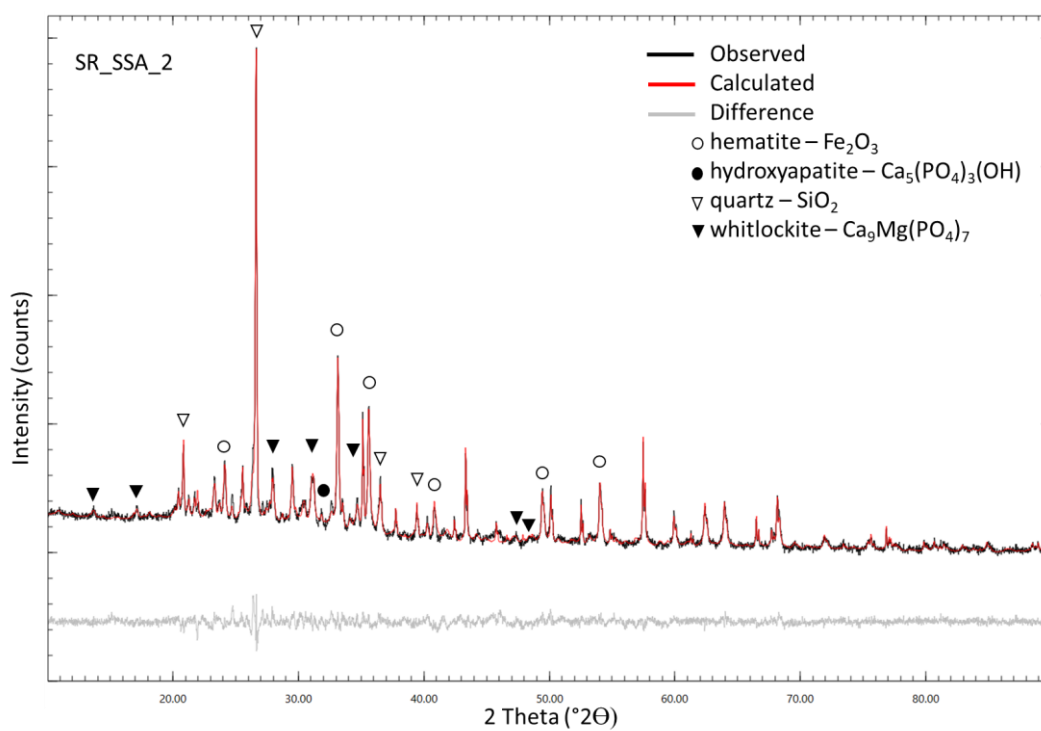


Figure 38. Rietveld refinement plot of SR_SSA_1.

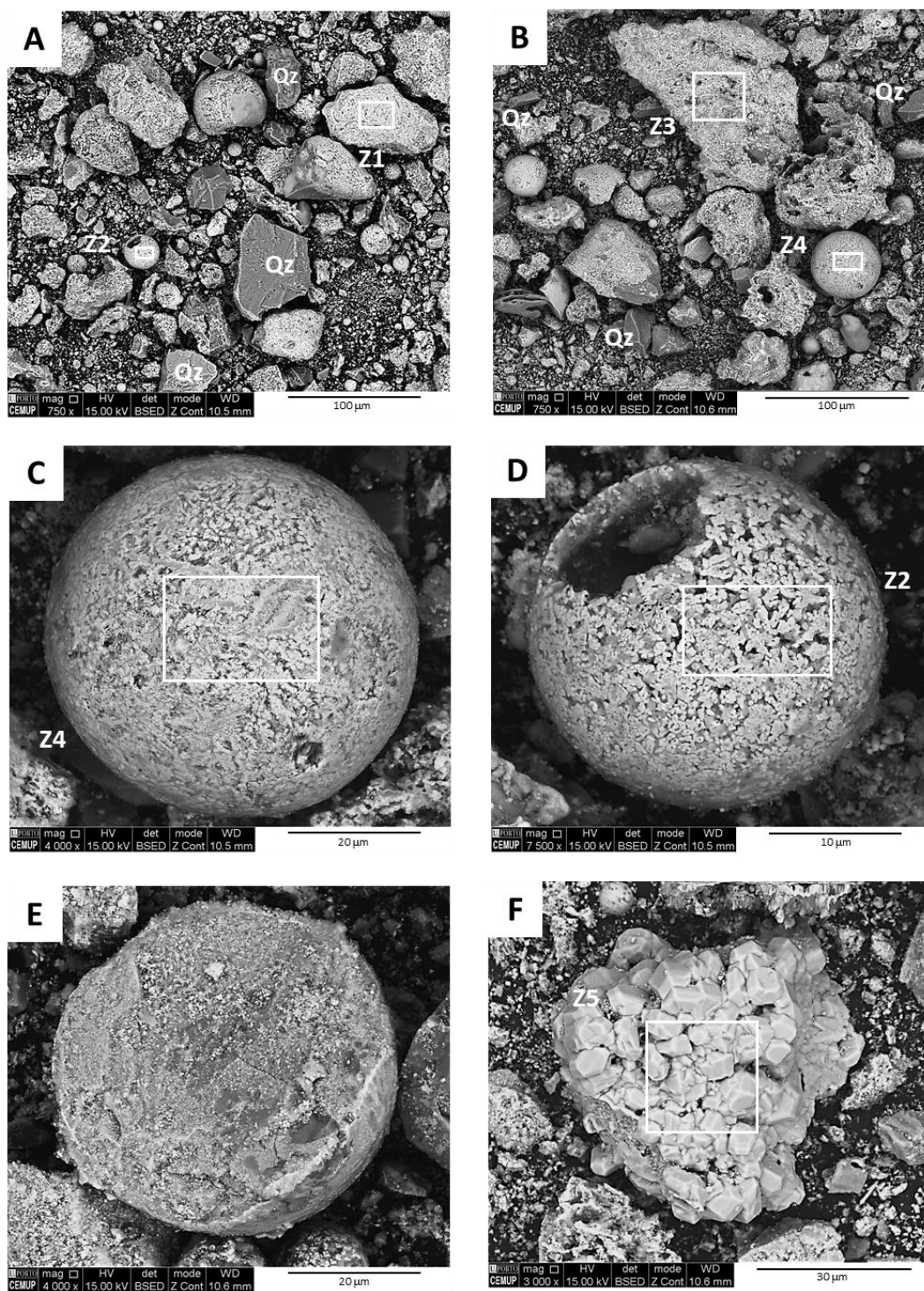


Figure 39. SEM-EDS analysis of as-collected samples solid residues: A) quartz crystals and P-Si-Fe spheres, spectra Z1 and Z2 (sample SR_SSA_1; BSE mode; 750x); quartz crystals and a wide particle of Si-P-Fe-Ca, spectra Z3 and Z4 (sample SR_SSA_2; BSE mode; 750x); C) P-Si-Fe sphere of $\approx 60 \mu\text{m}$ of diameter, spectra Z4 (sample SR_SSA_2; BSE mode, 4000x); D) P-Si-Fe sphere of $\approx 30 \mu\text{m}$ of diameter, spectra Z2 (sample SR_SSA_1; BSE mode, 7500x); E) half of a P-Si-sphere completely intact internally, showing no signs of structural degradation after leaching (SR_SSA_2; BSE mode; 4000x);

F) Calcium phosphate crystals structurally similar to whitlockite, spectra Z5(SR_SSA_2, BSE mode; 3000x).

Table 18. EDS semi-quantitative elemental analysis of solid residues of SSA_1 and SSA_2 after the NAC leaching.

Sample	SR_SSA_1		SR_SSA_2		
	Z1	Z2	Z3	Z4	Z5
Element	Wt%				
O	25.4	29.6	26.3	29.9	30.0
P	14.0	10.0	9.3	9.8	22.8
Ca	18.9	11.1	11.9	11.2	40.1
Na	0.2	-	-	-	-
Mg	1.2	0.6	0.9	1.0	2.0
K	2.6	0.9	1.3	1.7	-
Al	1.8	1.2	1.1	1.8	-
Si	5.8	7.3	5.9	8.3	-
Fe	29.2	38.4	42.3	35.4	1.5
Ti	0.8	1.0	1.1	0.9	-
Zn	-	-	-	-	3.7

3.5.3 MW-treated Sewage Sludge Ashes, Leachates, and Solid Residues

The following paragraphs are organized by reagent used. First, the results of the NAC leaching tests and the corresponding solid residues (SRs) for samples thermally treated with NaHCO_3 (Section 3.4.3.1) will be discussed, followed by those obtained for samples treated with KHCO_3 (Section 3.4.3.2). The extraction data of individual elements, with particular emphasis on phosphorus, is discussed at the same time for both of the temperature and samples because they present a general common trend. When necessary, distinctions between the two treatment temperatures and the two samples are highlighted. The chemical data are discussed in relation to the total content recalculated as previously explained.

This approach contributes to a deeper understanding of the operating principles of the microwave (MW) treatment, its strengths and limitations to be identified, and thereby provides a clear basis for future process development and improvement.

3.5.3.1 NaHCO₃ Leachates and Solid Residues

Table 19 reports the chemical analyses of the leachates after thermochemical treatment with NaHCO₃. For both samples at the two temperatures (800–1000 °C) employed in the thermal process. In Figures 40 and 41, the extraction of macronutrients and heavy metals after MW treatment is compared with the total amount after thermal treatment, as calculated according to equation (9)

*Table 19. Chemical analysis of NAC-leached SSA_1 and SSA_2 after the MW-treatment with NaHCO₃. Elements marked by * collected with TXRF, analyses for Cr (VI) with UV-vis. LOQ is the Limit of Quantification reported in Table 7.*

Sample NaHCO ₃	MW-Treated 800°C						MW-Treated 1000°C					
	SSA_1			SSA_2			SSA_1			SSA_2		
Element	mg/kg											
P	53259	±	4535	55761	±	4534	51782	±	4542	54756	±	4531
Na	50366	±	4535	51226	±	4534	47194	±	4542	43583	±	4531
K	2170	±	181	1940	±	181	1581	±	182	1324	±	181
Ca	101585	±	4535	99751	±	4534	99930	±	4542	90075	±	4531
Mg	2749	±	181	2055	±	181	3964	±	182	2418	±	181
S	12816	±	907	9803	±	907	15489	±	908	11000	±	906
Cd	n.d.											
Ti*	235	±	20	272	±	37	132	±	17	187	±	20
Cr*	96	±	6	114	±	14	138	±	12	126	±	7
Cr (VI)	91	±	9	107	±	11	126	±	13	132	±	13
Fe*	5442	±	65	7305	±	139	6979	±	227	6179	±	798
Ni*	46	±	12	27	±	7265	31	±	8	14	±	4
Cu*	50	±	5	58	±	17	68	±	10	52	±	10
Zn*	334	±	7	283	±	18	751	±	61	476	±	34
Pb*	29	±	2	40	±	10	38	±	6	20	±	10
As*	n.d.											

The total elemental contents after thermal treatment are lower than those of the as-collected material by approximately 9%. This indicates that, in the absence of volatilization, all elements are noticeably diluted by the addition of the reactive salt, resulting in a significant increase in the Na content.

As shown in Figure 40, phosphorus solubility after 800 °C thermal MW treatment increased significantly, reaching approximately 5.3–5.6% in solution, corresponding to extraction efficiencies of about 86.8% and 99.8% for SSA_1 and SSA_2, respectively. These are very significant values, particularly for SSA_2, where an almost complete extraction appears to occur at 800 °C. The treatment at 1000 °C also promoted the formation of a synthetic material containing highly soluble phosphorus, although to a slightly lesser extent than that observed at 800 °C. The phosphorus concentration in solution was 5.2 % and 5.5 %, with extraction efficiencies of approximately 83.7 % and 97.8 % for SSA_1 and SSA_2, respectively.

The solubility of phosphorus compounds is further supported by the quantitative phase analyses (QPA) in Table 20 and Figure 42 (showing the diffraction pattern of the SSA_1 solid residue). The analysis reveals that the previously abundant buchwaldite phase (over 20 wt%) has been completely leached, consistent with the marked increase of P in solution. Additionally, in the solid residue, the only P-crystalline phase present is the silicocarnotite (content below 1 wt% for all samples), corresponding at most to a crystalline P content of lower than 0.14 wt% (Table 20 - *SR_MW_SSA_1 at 800 °C*). The SEM–EDS images and spectra for the samples leached after 800 °C treatment (Figure 44, spectra in Table 21) and for the samples leached after 1000 °C treatment (Figure 45, spectra in Table 22) further confirm the very low P content in the solid residues. As illustrated, most of the particles exhibit a highly altered structure, with micrometric hollow areas and irregular honeycomb-like features corresponding to the zones formerly occupied by buchwaldite blebs, embedded within the silicate matrix. The particles analysed through EDS exhibit no measurable phosphorus content, or only traces with concentrations generally lower than 1 wt%, verifying the almost complete removal of P from the solid sample during the NAC leaching.

The other elements considered macronutrients exhibit different solubilities compared to the total amount that follows in these ranges (Figure 40): Ca 70–80%, K 30–50%, with the higher solubility exhibited at 800 °C for both samples, Mg 20-40%, and S 80-97% with the higher solubility shown at 1000 °C for both samples. The high Ca and Na concentrations in the leachate are mainly attributed to the dissolution of buchwaldite blebs, while the elevated S content

results from the conversion of anhydrite into thenardite and metathenardite, both highly soluble in water [123] and in neutral ammonium citrate.

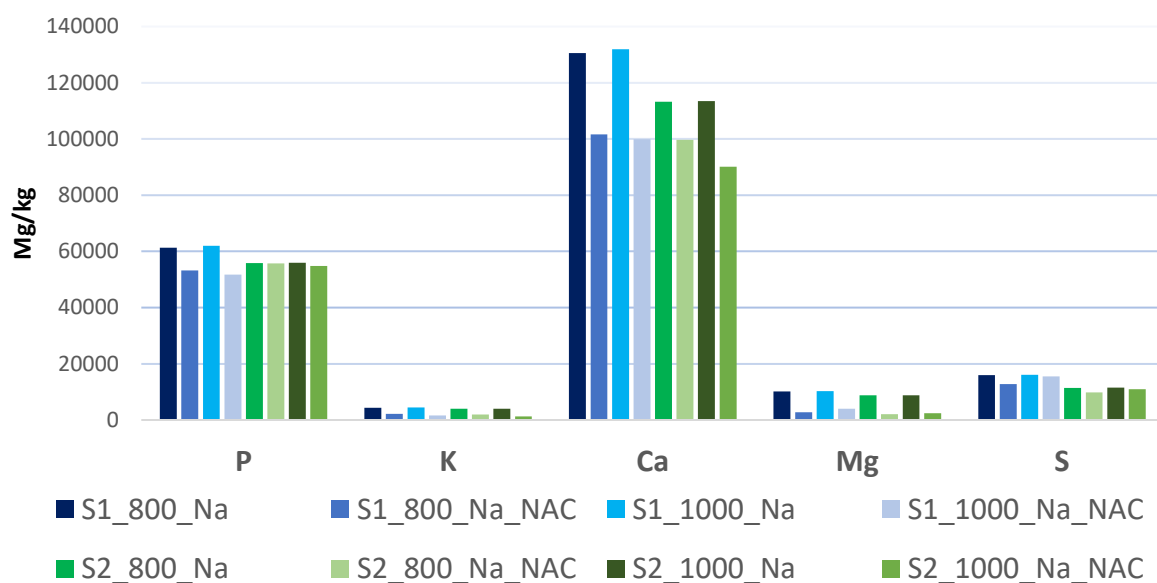


Figure 40. Comparison between the total content of macronutrients (SSA_1 and SSA_2) after the MW treatments and their solubility in NAC after the MW treatment with NaHCO₃ at 800 °C and 1000 °C.

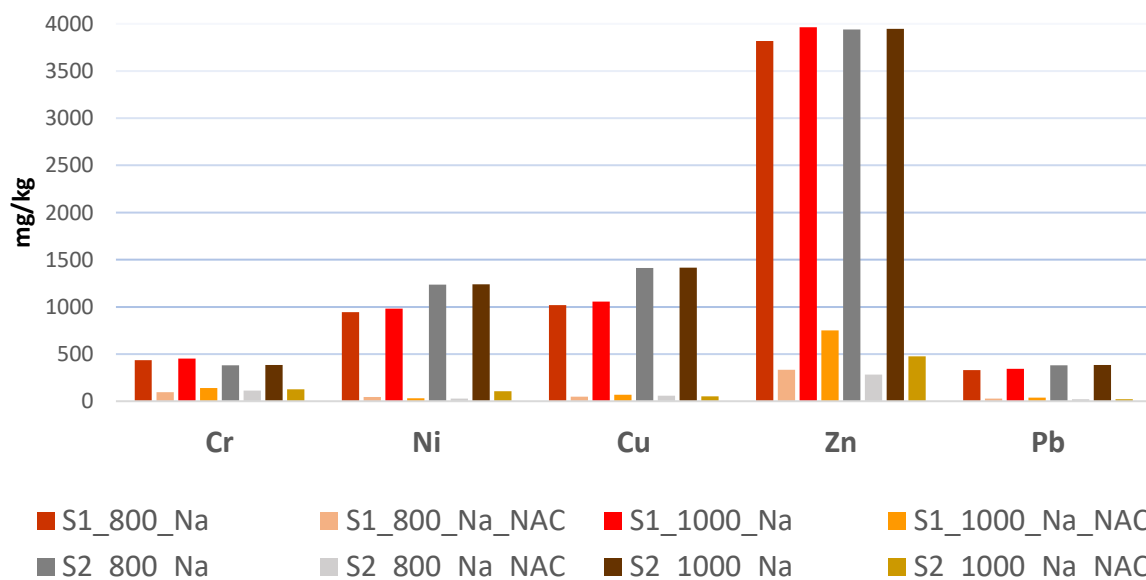


Figure 371. Comparison between the total content of heavy metals (SSA_1 and SSA_2) after the MW treatments and their solubility in NAC after the MW treatment with NaHCO₃ at 800 °C and 1000 °C.

The heavy metals Ni, Cu, Zn, and Pb exhibit a low solubility in NAC, being consistently lower than the 10% of the total after the treatment at 800 °C, while having values above this limit for Zn (12-18%) and Pb (11% only for SSA_1) after the treatment at 1000 °C (Figure 41). Cr, instead, presents a quite high solubility, approximately 20-30% of the total amounts at both temperatures, and, in addition, as reported in Table 19, the values of total Cr and Cr(VI) are very similar (e.g., 96 mg/kg total Cr and 91 mg/kg Cr(VI) for SSA_1), indicating that hexavalent chromium is the predominant species in solution. Before treatment, chromium was present in solution at concentrations of approximately 30 mg/kg, while Cr(VI) was below the detection limit (0.02 mg L^{-1}), confirming its absence in the untreated samples and suggesting its formation during the thermal process. The formation of Cr(VI) is a common feature observed in all samples treated under MW conditions and will be discussed in Section 3.5.4.

The presence of these metals is difficult, if not impossible, to describe using QPA or SEM-EDS data because we are accounting for elements present in quantities below 0.4%, which are difficult to detect with these techniques. Although using SEM micrographs (Figure 44A and 44D) and EDS spectra Z3, Z5, and Z9 (Table 21), the presence of Zn has been revealed to be bonded mostly in iron particles.

Table 20. QPA of the solid residue (SR) of SSA_1 and SSA_2 treated with NaHCO₃ after the NAC leaching, and the value of total crystalline P. R_{wp} is the refinement agreement factor; χ^2 is the goodness-of-fit statistic from the Rietveld refinement.

Sample		SR_MW_SSA_1		SR_MW_SSA_2	
Temperature (°C)		800	1000	800	1000
Cr. Phase	Chemical formula				
akermanite	$Ca_2Mg(Si_2O_7)$	5.1 (3)	8.1 (3)	5.4 (3)	8.9 (3)
albite	$Na(AlSi_3O_8)$	2.9 (1)	0.3 (1)	3.7 (2)	-
belite	Ca_2SiO_4	2.7 (3)	0.8 (1)	3.3 (3)	1.8 (3)
bredigite	$Ca_7Mg(SiO_4)_4$	0.8 (2)	0.4 (1)	0.4 (1)	-
gehlenite	$Ca_2Al(AlSiO_7)$	1.0 (3)	1.8 (3)	0.7 (1)	1.4 (4)
hedenbergite	$CaFeSi_2O_6$	1.8 (2)	2.2 (2)	1.8 (3)	1.9 (2)
hematite	Fe_2O_3	22.9 (5)	25.5 (5)	25.9 (5)	28.1 (5)
lazurite	$Na_3Ca(Al_3Si_3O_{12})S$	0.9 (1)	3.8 (2)	0.8 (1)	3.7 (2)
mackinawite	FeS	0.3 (1)	0.3 (1)	0.4 (1)	0.3 (1)
magnetite	Fe_3O_4	10.3 (2)	4.1 (1)	10.7 (2)	4.1 (1)
nepheline	$Na_3K(Al_4Si_4O_{16})$	7.0 (3)	3.3 (2)	8.9 (3)	3.7 (2)
quartz	SiO_2	5.6 (2)	0.5 (1)	5.6 (2)	0.8 (1)
rodolicoite	$Fe(PO_4)$	-	Tr	-	Tr
silicocarnotite	$Ca_5(PO_4)_2(SiO_4)$	0.9 (3)	0.5 (2)	0.8 (1)	0.4 (1)
thenardite	Na_2SO_4	1.4 (2)	-	1.1 (1)	-
titanite	$CaTiSiO_5$	-	0.4	-	0.7
Amorphous		36.7 (15)	48.0 (11)	30.5 (15)	44.2(11)
Cr. Phosphorus	P	0.14	0.06	0.11	0.08
R_{wp}		1.28	1.33	1.13	1.32
χ^2		1.28	1.31	1.36	1.29

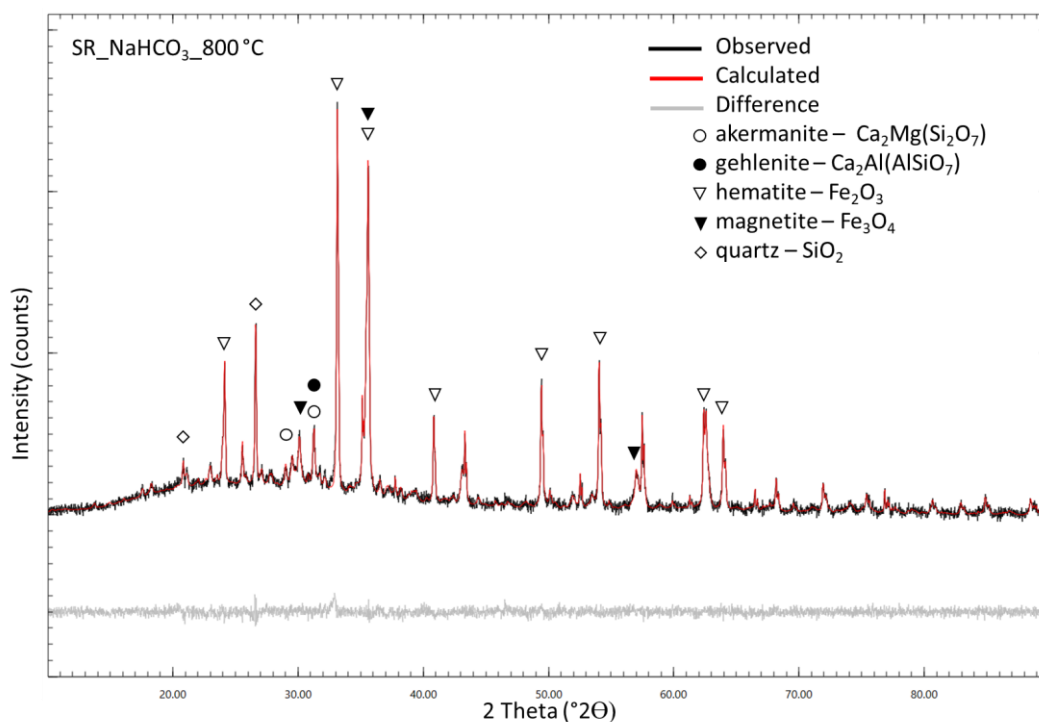


Figure 42. Rietveld refinement plot of the Solid Residue after the leaching in NAC on SSA_1 MW-treated with NaHCO_3 at 800 °C.

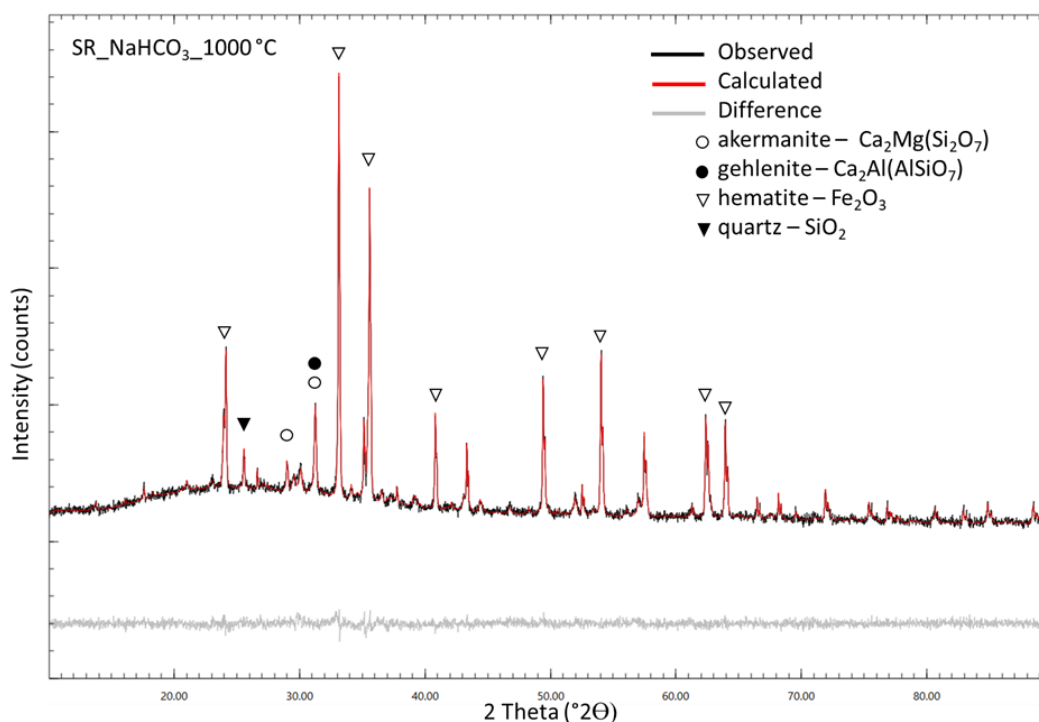


Figure 43. Rietveld refinement plot of the Solid Residue after the leaching in NAC on SSA_1 MW-treated with NaHCO_3 at 1000 °C.

Table 21. EDS semi-quantitative elemental analysis of solid residues of SSA_1 and SSA_2 after the MW treatment at 800 °C (assisted with NaHCO₃) and leached with NAC.

Sample	SR_SSA_1					SR_SSA_2				
NaHCO ₃ 800°C	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9	Z10
Element	wt %									
O	40.9	37.8	18.7	33.1	29.7	36.9	32.5	32.8	23.6	15.5
P	-	-	-	0.9	0.8	-	-	-	-	2.8
Ca	1.4	5.0	0.5	2.0	3.5	6.0	6.6	5.3	1.1	1.4
Na	7.8	7.5	0.9	2.9	1.5	4.4	6.1	5.8	1.4	1.3
Mg	0.7	1.7	2.6	0.5	5.9	0.9	3.0	1.9	3.4	0.6
K	4.8	2.6	0.8	4.0	-	3.5	1.7	2.1	0.9	-
Al	17.8	2.5	0.7	4.6	0.7	1.6	3.8	4.4	1.5	0.3
Si	23.9	24.8	2.7	28.5	1.7	29.9	16.3	17.7	4.2	1.6
Fe	2.8	18.1	68.6	22.2	54.8	15.6	29.0	28.7	59.9	4.3
Ti	-	-	1.2	1.3	-	0.7	1.0	1.3	0.8	-
Cl	-	-	-	-	-	0.4	-	-	-	-
Zn	-	-	3.3	-	1.5	-	-	-	3.2	
Th	-	-	-	-	-	-	-	-	-	4.6
U	-	-	-	-	-	-	-	-	-	1.5
La	-	-	-	-	-	-	-	-	-	12.4
Ce	-	-	-	-	-	-	-	-	-	41.4
Nd	-	-	-	-	-	-	-	-	-	12.4

The quantitative phase analysis (QPA), combined with SEM–EDS observations, provides a comprehensive overview for the classification of the solid residue (SR) and for its mineralogical and structural characterisation. As can be observed, the SR is dominated by a Si- and Fe-based chemistry, allowing it to be classified as a ferro siliceous powder.

Silicon-bearing crystalline phases are mainly represented by high-temperature silicates, including akermanite, belite, bredigite, and gehlenite, whereas iron is predominantly present in the form of hematite and magnetite. Although NAC effectively promoted the solubilisation of the phosphate-bearing crystalline phases, no evidence of the formation of new crystalline phases resulting from its interaction with the matrix was identified. The X-ray diffraction analysis did not reveal the appearance of additional diffraction peaks nor systematic shifts in peak positions that could be ascribed to the crystallisation of secondary phosphate or NAC-related compounds. This indicates that the interaction between NAC and the material primarily led to the dissolution of the original phosphate phases, rather than their transformation into new

long-range-ordered crystalline structures. Consequently, the action of NAC can be interpreted as a chemical interaction occurring predominantly in solution, without stabilisation of new crystalline phases under the investigated experimental conditions. Finally, the amorphous fraction accounts for approximately 30–50 wt% of the material after leaching (Table 20). This represents an increase of about 10–15 wt% compared to the material after the thermal treatment alone (Table 11), suggesting a limited tendency of the amorphous component of this matrix to undergo solubilisation in NAC. This behaviour appears to be in contrast with the findings discussed in Chapter 2 (Section 2.3.6), where the amorphous phase played a key role in promoting phosphorus solubilisation and release.

However, the present system differs substantially from those previously discussed, as it involves distinct matrices and different leaching media. These differences contribute to the observed behaviour and highlight the intrinsic complexity of phosphate-bearing compounds, whose interactions with solvents strongly depend on the specific chemical environment and on the crystallinity of the phases involved.

SEM-EDS micrographs revealed particular and interesting microstructural features of the SRs, which are characterised by particles with relatively homogeneous morphology and size distribution, generally below 100 μm . Moreover, the honeycomb-like structure, as briefly mentioned in the previous section, suggests the potential for a secondary and direct reuse of the SR

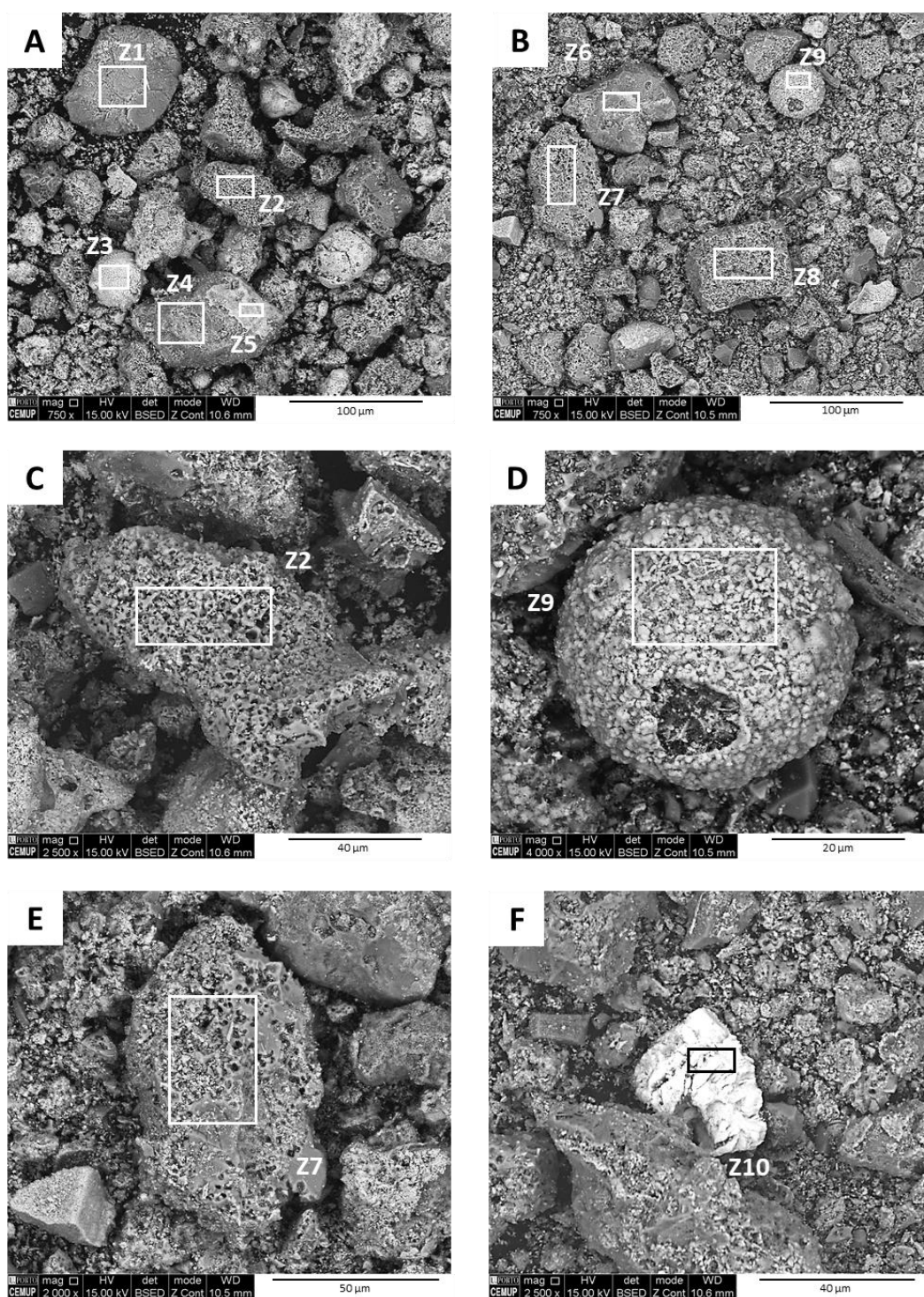


Figure 44. SEM-EDS analysis of MW-treated (800 °C and NaHCO_3) and NAC-leached samples solid residues: A) low magnification of the solid residue, spectra Z1, Z2, Z3, Z4, Z5 (sample SR_NaHCO_3 _800 of SSA_1; BSE mode; 750x); B) low magnification of the solid residue, spectra Z6, Z7, Z8, Z9 (sample SR_NaHCO_3 _800 of SSA_2; BSE mode; 750x); C) high magnification of a particles showing honeycomb structures, spectra Z2 (sample SR_NaHCO_3 _800 of SSA_1; BSE mode, 2500x); D) altered P-Si-Fe sphere of $\approx 30 \mu\text{m}$ of diameter, spectra Z9 (sample SR_NaHCO_3 _800 of SSA_2; BSE mode, 4500x); E) high magnification of a particles showing honeycomb structures, spectra Z7 (sample SR_NaHCO_3 _800

of SSA_1; BSE mode, 2500x); F) Monazite submicrometric crystal, spectra Z10 (sample SR_NaHCO₃_800 of SSA_2; BSE mode; 2500x).

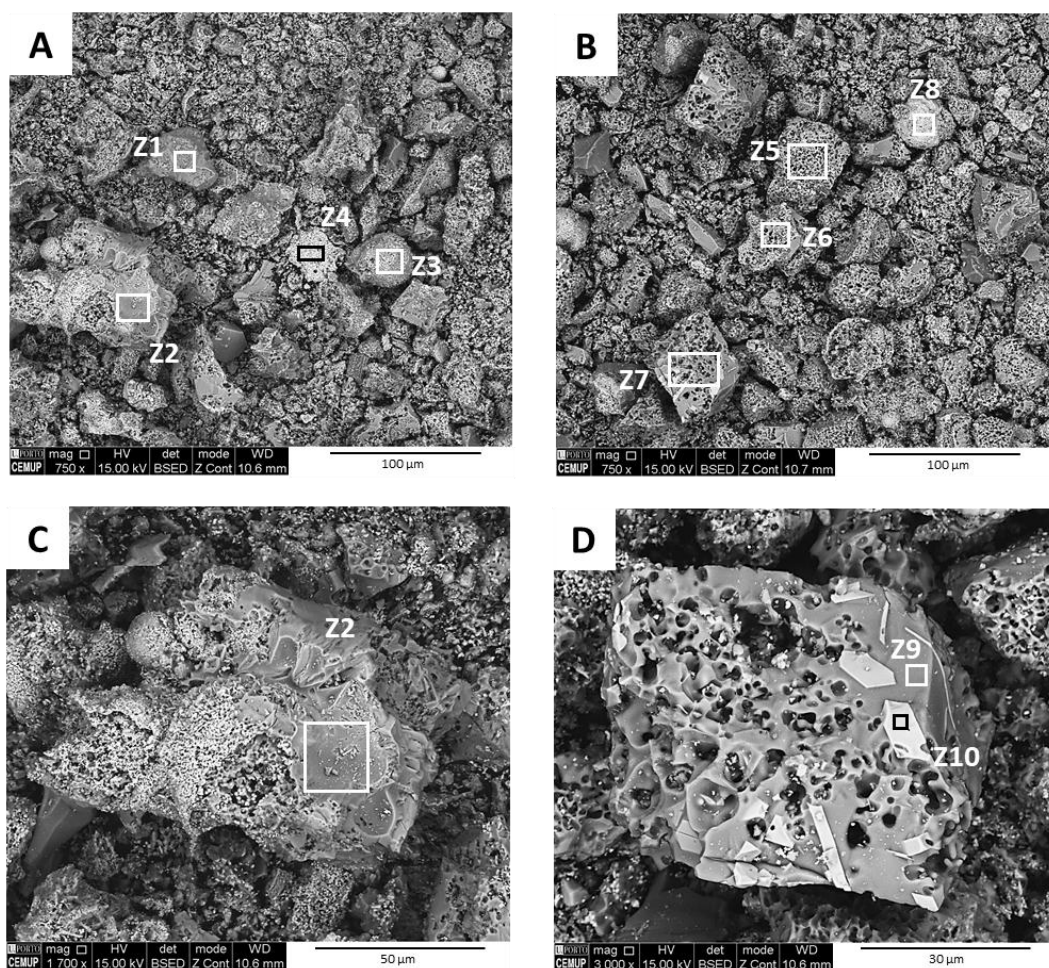


Figure 45. SEM-EDS analysis of MW-treated (1000 °C and NaHCO₃) and NAC-leached samples solid residues: A) low magnification of the solid residue, spectra Z1, Z2, Z3, Z4 (sample SR_NaHCO₃_1000 of SSA_1; BSE mode; 750x); B) low magnification of the solid residue, spectra Z5, Z6, Z7 (sample SR_NaHCO₃_1000 of SSA_2; BSE mode; 750x); C) high magnification of a particles showing honeycomb structures, spectra Z2 (sample SR_NaHCO₃_800 of SSA_1; BSE mode, 1700x); D) high magnification of a particles showing honeycomb structures, spectra Z9, Z10 (sample SR_NaHCO₃_800 of SSA_2; BSE mode, 3000x).

Table 22. EDS semi-quantitative elemental analysis of solid residues of SSA_1 and SSA_2 after the MW treatment at 1000 °C (assisted with NaHCO₃) and NAC leach.

Sample	SR_SSA_1					SR_SSA_2				
NaHCO ₃ 1000 °C	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9	Z10
Element	wt %									
O	39.9	42.2	24.9	17.5	22.1	26.7	33.4	25.1	41.4	25.2
P	-	-	-	-	0.3	0.2	0.5	3.3	0.4	-
Ca	4.7	14.8	1.9	0.8	11.4	4.9	9.0	7.7	9.6	-
Na	9.9	4.5	3.4	0.5	2.5	6.9	6.2	1.5	7.7	-
Mg	1.0	0.7	0.9	0.7	2.0	1.2	1.6	0.7	1.7	0.6
K	2.7	2.7	2.0	-	1.3	1.6	1.8	0.4	1.7	-
S	0.8	0.2	-	-	-	0.3	-	0.2	0.2	-
Al	8.8	1.9	2.7	0.5	2.1	2.4	4.0	1.6	2.1	-
Si	24.3	24.9	10.7	1.8	13.4	14.6	19.1	2.8	22.9	-
Fe	7.0	7.9	52.3	76.9	43.8	40.4	23.6	55.5	11.6	72.8
Ti	-	-	1.2	1.2	1.1	0.7	0.9	1.0	0.6	1.4
Cl	0.9	0.4	-	-	-	0.2	-	0.3	0.1	-

3.5.3.2 KHCO₃ Leachates and Solid Residues

Table 23 reports the chemical composition of the leachates obtained after thermochemical treatment with KHCO₃ for both samples treated at 800 and 1000 °C. Figures 46 and 47 compare the extracted amounts of macronutrients and heavy metals with their corresponding calculated total contents after the MW-treatment (Equation 9). The total elemental concentration at both temperatures (800 – 1000 °C) is lower than that of the as-collected material due to a dilution effect associated with the addition of the reactive salt and the resulting increase in alkali metal content (Na).

Table 23. Chemical analysis of NAC-leached SSA_1 and SSA_2 after the MW-treatment with KHCO_3 . Elements marked by * collected with TXRF, analyses for Cr (VI) with UV-vis. LOQ is the Limit of Quantification reported in Table 7.

Sample NaHCO ₃	MW-Treated 800°C						MW-Treated 1000°C					
	SSA_1			SSA_2			SSA_1			SSA_2		
Element	mg/kg											
P	39562	±	4530	46547	±	4496	34982	±	4510	41034	±	4501
Na	1008	±	45	1158	±	45	1163	±	45	978	±	45
K	63668	±	1812	64857	±	1799	46573	±	1804	48425	±	1801
Ca	80255	±	4530	88391	±	4496	67816	±	4510	80583	±	4501
Mg	3169	±	181	3148	±	180	1540	±	180	1593	±	180
S	13770	±	906	12536	±	899	13386	±	902	8517	±	900
Cd	n.d.											
Ti*	388	±	79	558	±	224	471	±	83	290	±	30
Cr*	81	±	8	102	±	33	164	±	5	149	±	23
Cr (VI)	77	±	8	109	±	11	158	±	16	135	±	13
Fe*	8883	±	252	11130	±	3304	11968	±	208	12789	±	222
Ni*	42	±	9	100	±	88	26	±	2	21	±	2
Cu*	78	±	9	89	±	15	36	±	8	26	±	11
Zn*	322	±	60	356	±	55	232	±	33	206	±	9
Pb*	43	±	22	61	±	15	52	±	22	42	±	29
As*	n.d.											

As shown in Table 23, phosphorus solubility after microwave-assisted treatment at 800 °C, reaches concentrations of about 3.9–4.7 % in solution. These values correspond to extraction efficiencies of approximately 66.8% and 87.8% for SSA_1 and SSA_2, respectively. The treatment at 1000 °C also promoted the formation of compounds containing higher soluble phosphorus, although to a slightly lower extent, with solution concentrations of 3.5–4.1% and extraction efficiencies of about 57.8% and 76.3% for SSA_1 and SSA_2, respectively. When KHCO_3 is employed as an alkaline additive, the overall phosphorus extraction is significantly lower compared to NaHCO_3 , although the same trend is preserved. In particular, the SSA_2 sample exhibits a higher P extraction, with a difference of approximately 20% after treatment with KHCO_3 . This behaviour highlights the presence of substantial differences in the initial

matrix, which promote the formation of distinct phosphate phases characterised by markedly different phosphorus solubility.

The phosphorus solubility is further supported by the quantitative phase analysis (QPA) reported in Table 24 and by the XRD pattern of the SSA_1 solid residue shown in Figures 48 and 49. The analysis indicates that the KCaPO_4 phase, initially present, is completely removed during NAC leaching, consistent with the marked increase in phosphorus concentration in solution. In the solid residues, anyway, a considerable amount of hydroxyapatite and whitlockite is found. These two phases did not undergo complete transformation during microwave-assisted treatment in combination with KHCO_3 . Furthermore, some traces of silicocarnotite are found in the solid residues. The combination of these P-bearing crystalline phases accounts for approximately 1.14-2.13 of crystalline P (Table 24).

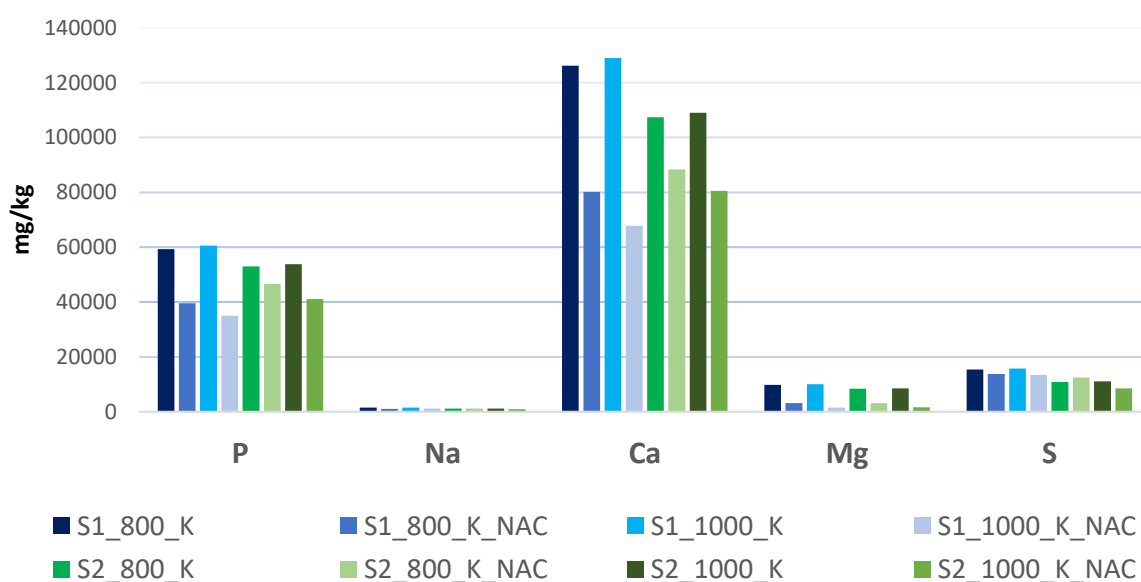


Figure 46. Comparison between the total content of macronutrients (S1 = SSA_1 and S2 = SSA_2) after the MW treatments and their solubility in NAC after the MW treatment with KHCO_3 at 800 °C and 1000 °C.

SEM–EDS micrographs and spectra of samples leached after treatment at 800 °C (Figure 50 and Table 25) and 1000 °C (Figure 51 and Table 25) generally confirm a low phosphorus content in the solid residues, with P values below 1 wt%. Exceptions are spectrum Z4 (Figure 50 D) representing a crystal of calcium phosphate, probably hydroxyapatite, according to the elongated tabular crystals shape and spectra and Z1 and Z6 (Figure 51A and 51B), over larger areas compared to the Z4 spectrum, specifically in regions where clear signs of leaching are visible and where the characteristic honeycomb-like structures generated by the dissolution of

KCaPO₄ can be observed. In these areas, higher elemental values for P and Ca were detected. However, these values do not reflect the presence of residual KCaPO₄ but the presence of material that remained untransformed, in which phosphorus is still associated with phases such as whitlockite and hydroxyapatite. This observation further confirms, in agreement with the analyses performed on the microwave-treated sample discussed in the previous section, the lower capability of the saline reagent KHCO₃ to effectively promote the transformation of phosphate phases. Still, most particles exhibit a highly altered morphology characterised by micrometric hollow features and irregular honeycomb-like structures, therefore, despite the inability to quantify KCaPO₄ through QPA, its presence appears to be appreciable, although lower compared to buchwaldite. The latter has generated more extensive honeycomb-like voids throughout the matrix, in areas where no crystals containing significant amounts of phosphorus were detected.

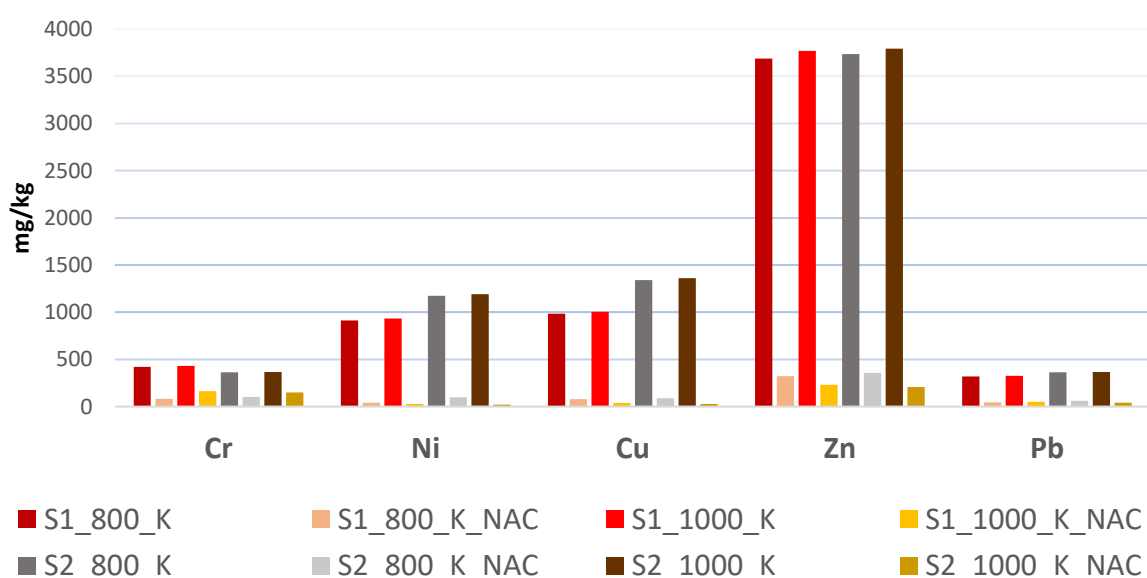


Figure 47. Comparison between the total content of heavy metals (SSA_1 and SSA_2) after the MW treatments and their solubility in NAC after the MW treatment with KHCO₃ at 800 °C and 1000 °C.

The other macronutrients show different solubility behaviours relative to their total contents. Calcium exhibits extraction efficiencies of 50-80%, sodium 65–100%, magnesium 15–40% and sulfur 77-90%, with the highest solubility showed at 800 °C and constantly enhanced for sample SSA_2. The value of S for sample SSA_2 treated at 1000 °C exceeds the total sulfur content (115%), likely due to analytical uncertainty. The high calcium and potassium concentrations in the leachates (Table 23) are mainly attributed to the dissolution of KCaPO₄ blebs, whereas the elevated sulfur content results from the conversion of anhydrite into arcanite, which presents

high solubility in various solvents [124] and also in neutral ammonium citrate. Arcanite is still present in all the solid residues (Table 24) in amounts lower than 4 wt%. This behaviour is likely attributable to the reprecipitation of dissolved species during the drying stage of the solid residues.

Heavy metals such as Ni, Cu, and Zn generally exhibit low solubility in NAC after thermal treatment, remaining below 10% of the total content at both temperatures (Figure 47). Only Pb shows a solubility ranging from 11-16 % of the total calculated amount. Chromium, as previously observed, exhibits relatively high solubility, accounting for approximately 20–40% of the total chromium content, with the highest values observed after the 1000 °C thermal treatment. Here, as reported in Table 23, total chromium and Cr(VI) concentrations are very similar, indicating that hexavalent chromium is the dominant chromium species in solution. Prior to treatment, chromium was present at approximately 30 mg/kg, while Cr(VI) was below the detection limit, suggesting that it formed during the thermal process. This behaviour is systematically observed in all samples treated under microwave conditions and is discussed in Section 3.5.4.

Table 24. QPA of the solid residue (SR) of SSA_1 and SSA_2 treated with KHCO_3 after the NAC leaching, and the value of total crystalline P. R_{wp} is the refinement agreement factor; χ^2 is the goodness-of-fit statistic from the Rietveld refinement.

Sample		MW_SSA_1		MW_SSA_2	
Temperature (°C)		800	1000	800	1000
Cr. Phase	Chemical formula				
akermanite	$\text{Ca}_2\text{MgSi}_2\text{O}_7$	4.6 (2)	5.1 (2)	2.4 (1)	3.8 (1)
albite	$\text{NaAlSi}_3\text{O}_8$	5.8 (4)	-	5.8 (2)	-
arcanite	K_2SO_4	2.7 (1)	1.8 (2)	0.9 (1)	3.5 (1)
belite	Ca_2SiO_4	5.9 (3)	5.3 (2)	3.2 (2)	4.9 (3)
bloedite	$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	4.5 (2)	8.3 (4)	3.2 (2)	12.1 (5)
ferrosilite	FeSiO_3	1.0 (2)	-	3.8 (2)	-
gehlenite	$\text{Ca}_2\text{Al}(\text{AlSiO}_7)$	1.0 (2)	-	0.6 (1)	2.8 (1)
hematite	Fe_2O_3	20.5 (4)	10.5 (2)	15.7 (2)	12.5 (3)
hydroxyapatite	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	6.2 (2)	5.9 (2)	4.5 (1)	7.8 (2)
langbeinite	$\text{K}_2\text{Ca}_2(\text{SO}_4)_3$	7.8 (2)	10.6 (3)	3.7 (1)	11.1 (3)
leucite	$\text{K}(\text{AlSi}_2\text{O}_6)$	wt%	2.5 (3)	3.8 (2)	4.0 (2)
magnetite	Fe_3O_4	6.5 (2)	6.2 (2)	5.9 (1)	9.7 (3)
periclase	MgO	-	-	-	2.1 (1)
portlandite	$\text{Ca}(\text{OH})_2$	2.1 (1)	1.4 (1)	1.5 (1)	1.6 (1)
quartz	SiO_2	13.9 (4)	4.8 (2)	13.2 (3)	4.5 (2)
rodolicoite	FePO_4	-	1.9 (1)	-	-
rutile	TiO_2	0.2 (1)	0.5 (1)	0.4 (1)	1.4 (1)
silicocarnotite	$\text{Ca}_5(\text{PO}_4)_2(\text{SiO}_4)$	trace	trace	trace	trace
titanite	$\text{CaTi}(\text{SiO}_4)\text{O}$	trace	1.2 (1)	trace	3.9 (1)
whitlockite	$\text{Ca}_9\text{Mg}(\text{PO}_4)_7$	2.4 (1)	3.1 (1)	1.5 (1)	1.2 (1)
amorphous		13.4 (17)	29.6 (15)	29.7 (11)	12.5 (20)
Cr. Phosphorus	P	1.63	2.13	1.14	1.69
R_{wp}		1.82	1.88	1.69	2.24
χ^2		1.99	2.53	1.77	2.79

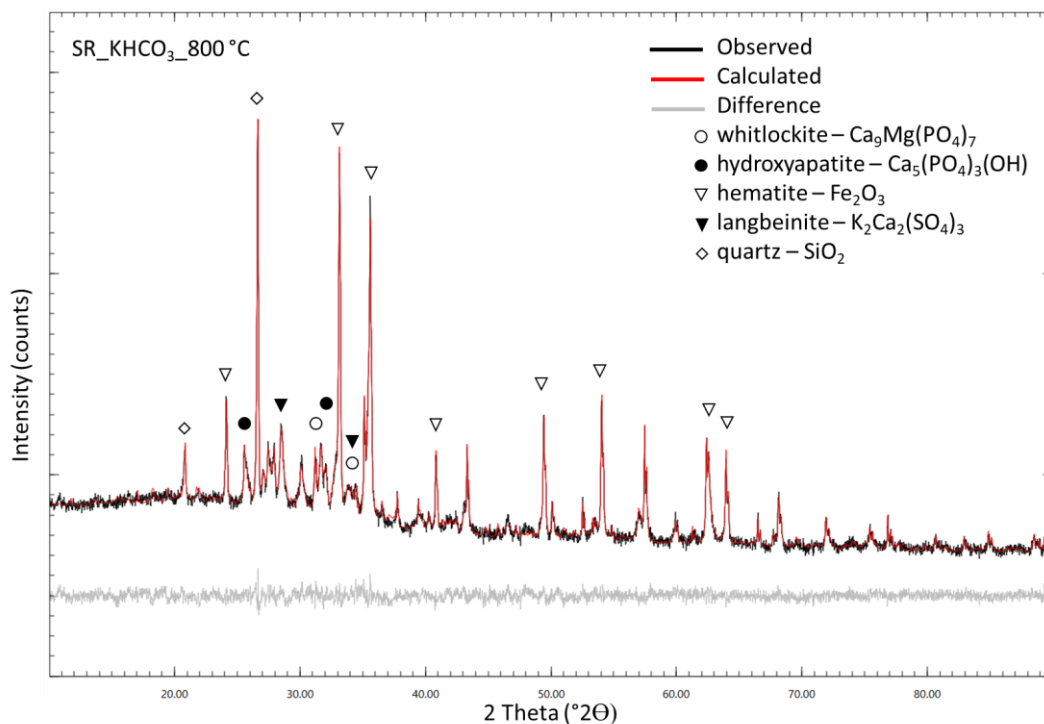


Figure 48. Rietveld refinement plot of the Solid Residue after the leaching in NAC on SSA_1 MW-treated with KHCO_3 at 800 °C.

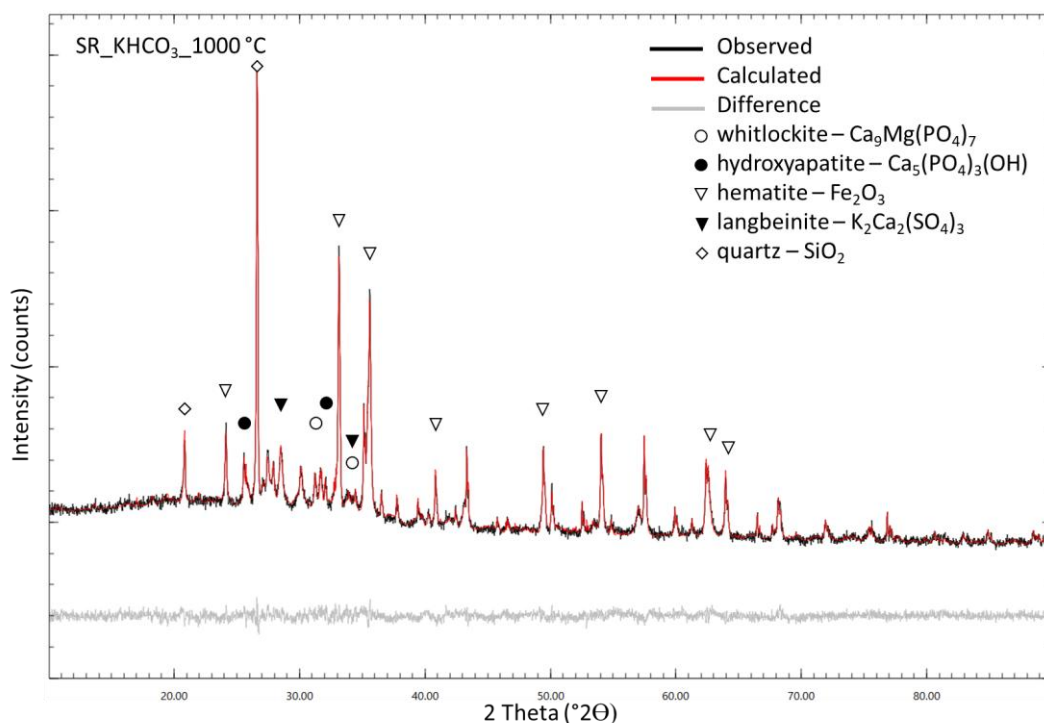


Figure 49. Rietveld refinement plot of the Solid Residue after the leaching in NAC on SSA_2 MW-treated with KHCO_3 at 800 °C.

The combined QPA (Table 24 and Figures 48-49 for the solid residues) and SEM-EDS analyses enable to classify the solid residues as ferro-siliceous powders characterised by a Si- and Fe-rich composition. The silicate fraction is mainly composed of high-temperature phases such as akermanite, belite, and gehlenite, together with leucite, which occurs in appreciable amounts (~ 5 wt%) and becomes more abundant after treatment at 1000 °C. Also, high quantities of albite are detected on the SRs after the 800 °C thermal treatment (≈ 5 -6 wt%). Iron-bearing phases are dominated by hematite and magnetite, whose combined abundance approaches ≈ 25 wt%, confirming the strong iron enrichment of the residual matrix.

Despite NAC's effectiveness in promoting the dissolution of KCaPO_4 , the original phosphates remain partially preserved in SRs. Hydroxyapatite remains the dominant phosphate phase, while whitlockite is detected in smaller amounts. No evidence of newly formed crystalline phases associated with secondary phosphates or NAC interactions is observed. XRD patterns show neither additional diffraction peaks nor systematic peak shifts, indicating that NAC mainly enhances the dissolution of phosphate phases into the liquid phase rather than promoting the formation of new crystalline compounds. SEM-EDS observations indicate that the solid residues consist of particles generally smaller than 100 μm . However, differences in particle size distribution are observed as a function of treatment temperature. After treatment at 1000 °C, particles appear slightly coarser, with a higher proportion of grains approaching ≈ 100 μm , whereas the residue obtained after treatment at 800 °C is characterised by generally finer particles, more frequently closer to ≈ 10 μm .

The honeycomb-like microstructure is observed in several particles, indicating localized dissolution processes. However, since phosphorus was not completely extracted, the residual material still contains phosphate phases. Therefore, despite the presence of these porous structures, the residues may represent a potential secondary resource for further phosphorus recovery or extraction.

Table 25. EDS semi-quantitative elemental analysis of solid residues of SSA_1 and SSA_2 after the MW treatment at 800 °C and 1000 °C (assisted with KHCO₃) and NAC leach.

Sample	SR_KHCO3_800 °C				SR_KHCO3_100 °C					
KHCO ₃	Z1	Z2	Z3	Z4	Z1	Z2	Z3	Z4	Z5	Z6
Element	wt %									
O	15.8	25.6	25.7	24.0	24.7	31.3	27.5	29.0	27.2	21.2
P	1.2	0.2	-	16.7	4.7	-	0.3	0.4	0.5	6.4
Ca	4.4	0.8	2.8	46.5	9.0	2.6	2.2	2.7	3.7	15.3
Na	-	0.2	-	-	0.2	-	0.4	-	-	-
Mg	0.7	3.8	1.0	-	2.5	1.3	4.0	1.0	1.3	0.8
K	5.7	9.8	22.8	3.6	7.6	21.3	11.3	21.5	21.0	6.6
S	-	-	-	-	-	-	-	-	-	-
Al	1.6	2.6	3.8	-	1.4	2.2	4.1	7.6	3.9	1.7
Si	4.8	8.4	17.9	3.8	4.2	23.4	8.2	14.4	21.6	5.7
Fe	64.5	47.4	25.3	4.9	43.0	17.1	39.6	22.1	20.8	41.2
Ti	1.4	1.1	0.7	-	2.7	0.9	2.6	1.3	-	1.1
Cl	-	-	-	0.5	-	-	-	-	-	-
Mn	-	-	-	-	0.8	-	1.0	-	-	-

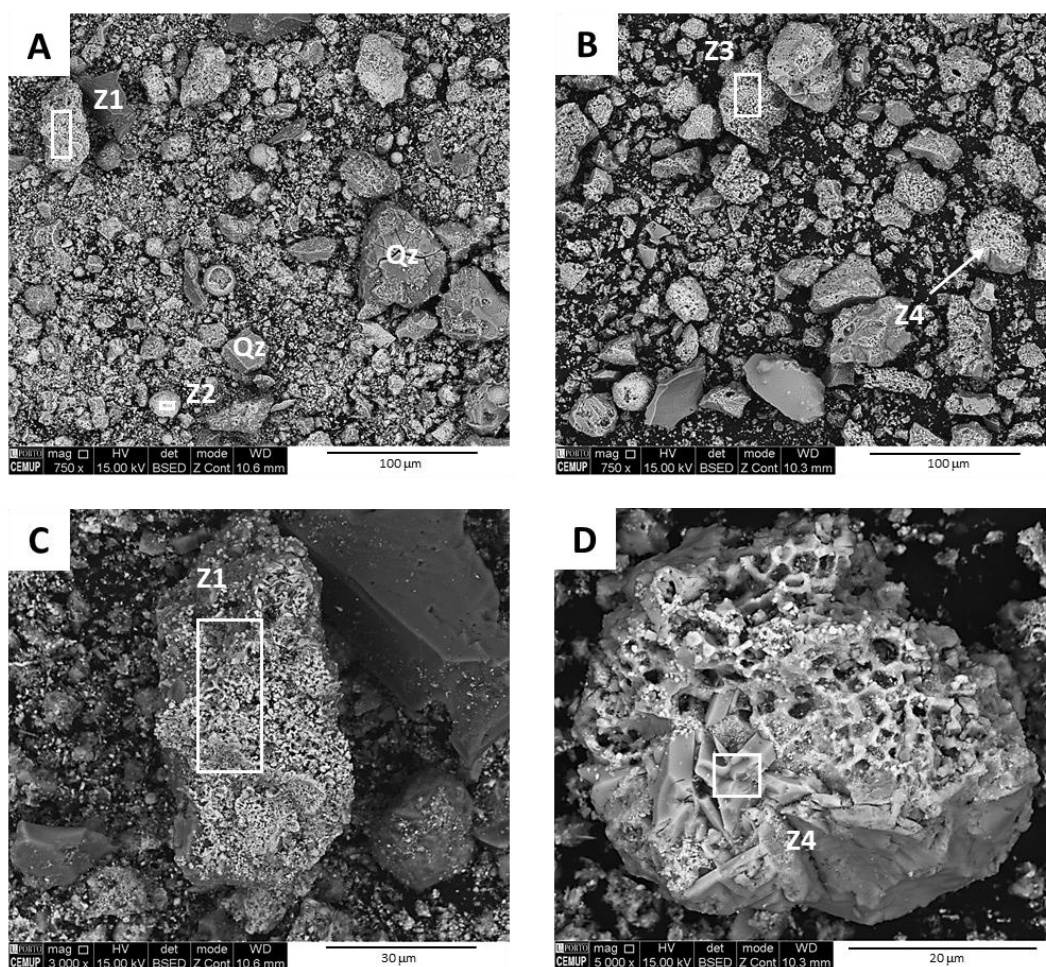


Figure 50. SEM-EDS analysis of MW-treated (800 °C and KHCO_3) and NAC-leached samples solid residues: A) low magnification of the solid residue, spectra Z1, Z2 (sample SR_KHCO_3_800 of SSA_1; BSE mode; 750x); B) low magnification of the solid residue, spectra Z4, Z5 (sample SR_KHCO_3_800 of SSA_2; BSE mode; 750x); C) high magnification of a particles showing faint honeycomb structures, spectrum Z1 (sample SR_KHCO_3_800 of SSA_1; BSE mode, 3000x); D) high magnification of a particles showing more marked honeycomb structures and hydroxyapatite crystals, spectrum Z4 (sample SR_KHCO_3_800 of SSA_2; BSE mode, 5000x).

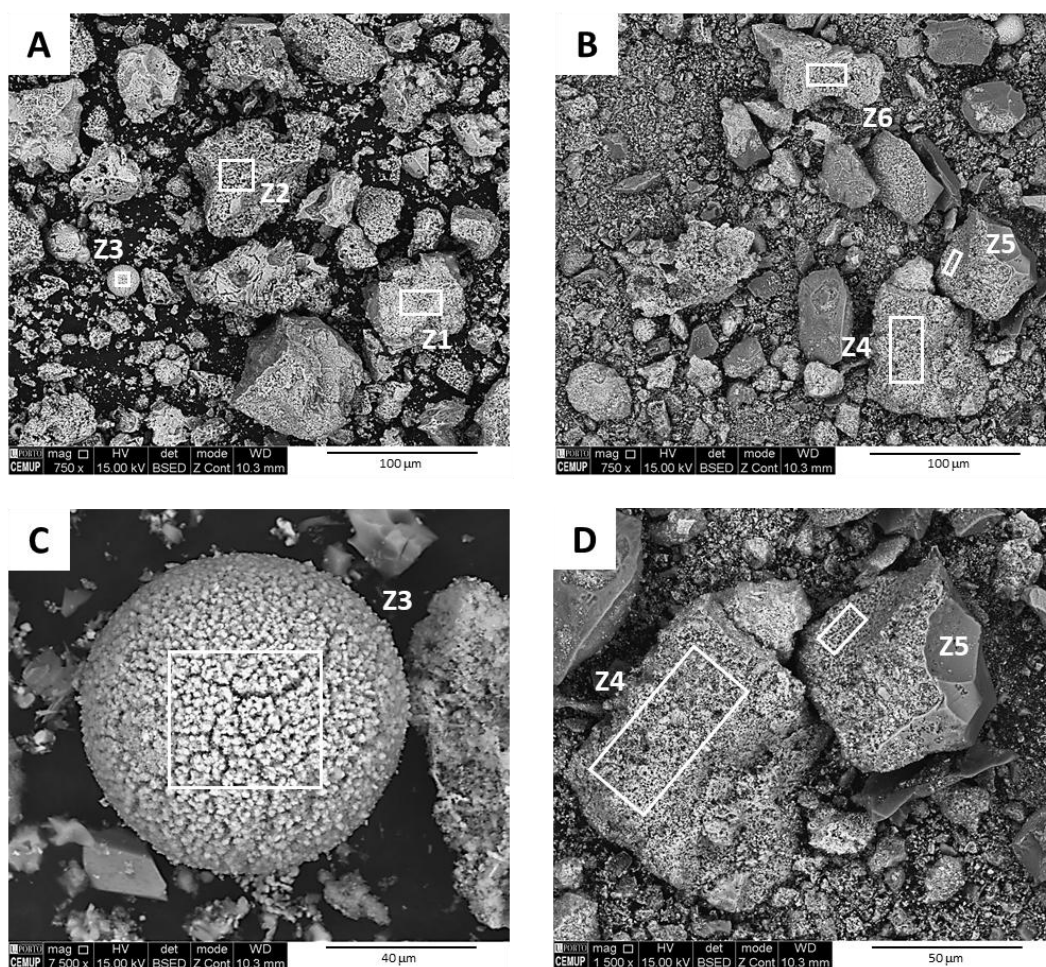


Figure 51. SEM-EDS analysis of MW-treated (1000 °C and KHCO₃) and NAC-leached samples solid residues: A) low magnification of the solid residue, spectra Z1, Z2 and Z3 (sample SR_KHCO₃_1000 of SSA_1; BSE mode; 750x); B) low magnification of the solid residue, spectra Z4, Z5 and Z6 (sample SR_KHCO₃_1000 of SSA_2; BSE mode; 750x); C) high magnification of a P-Si-Fe sphere showing slight alterations, spectrum Z3 (sample SR_KHCO₃_800 of SSA_1; BSE mode, 7500x); D) high magnification of a particles showing more honeycomb structures , spectra Z4 and Z5 (sample SR_KHCO₃_800 of SSA_2; BSE mode, 5000x).

3.5.4 Integrated Evaluation of Phosphorus Enhancement and Metal Solubilization in Alkali-Activated Sewage Sludge Ash

This section provides an integrated evaluation of phosphorus solubilization and metal mobilization in sewage sludge ash (SSA) following alkali activation with sodium and potassium bicarbonate. The results obtained for the treated samples are compared with those of the untreated ashes to assess the effectiveness of thermochemical treatment in enhancing phosphorus availability and to evaluate the potential release of critical elements.

Particular attention is given to phosphorus, the primary target element for resource recovery, and to hexavalent chromium (Cr(VI)), given its environmental relevance and potential implications for the reuse of treated materials. The combined interpretation of leaching results and mineralogical observations enables a critical assessment of the influence of alkaline reagents on both phosphorus-bearing phases and chromium speciation.

The comparison between untreated SSA and the materials treated with NaHCO_3 and KHCO_3 provides insight into the mechanisms governing phosphorus transformation and metal solubilization during the microwave-assisted thermochemical process.

3.5.4.1 Phosphorus Transformation and Solubilization in Alkali-Activated Sewage Sludge Ash

The untreated samples exhibited a phosphorus extraction efficiency of approximately 20% of the total phosphorus content for both SSAs matrices investigated.

Following thermochemical treatment with NaHCO_3 , a significant increase in phosphorus extraction was observed. For SSA_1, the extraction efficiency increased by approximately 60–63%, reaching values of about 84–87%, with slightly higher extraction observed for the sample treated at 800 °C. For SSA_2, the increase was even more pronounced, with an improvement of approximately 80%, resulting in almost complete phosphorus extraction from the thermochemically treated matrix following leaching in NAC. In particular, extraction efficiencies of 99.8% at 800 °C and 97.8% at 1000 °C were measured.

Although the enhancement in phosphorus availability is substantial for both matrices, a clear difference is observed between the two SSA samples, despite their similar overall composition. This difference can be interpreted by combining the QPA results obtained for the microwave-treated samples with the values of crystalline phosphorus quantified by XRD and the recalculated total phosphorus content after dilution with NaHCO_3 and subsequent thermochemical treatment and mass loss, as explained in section 3.5.

As reported in Table 11, the crystalline phosphorus content determined for SSA_2 is only slightly lower than the recalculated total phosphorus content of the MW-treated matrix, with differences of approximately 0.33 wt% for the sample treated at 800 °C and 0.59 wt% for the sample treated at 1000 °C. This indicates that, within the uncertainty associated with the measurements, nearly all the phosphorus present in the SSA_2 system is hosted in crystalline phases.

More specifically, almost the entire crystalline phosphorus fraction, except a very small portion always below 0.11 wt% (value reported in Table 20 for the SR at 800 °C of SSA_2), is associated with the buchwaldite phase, which exhibits very high solubility in NAC. This indicates that, in the SSA_2 system, the sodium-based reagent effectively promotes the transformation of phosphorus originally contained in phases such as whitlockite, hydroxyapatite, and the amorphous fraction into buchwaldite. Therefore, the newly formed phase is almost completely dissolved during NAC leaching, explaining the nearly quantitative phosphorus extraction observed.

A different behaviour was observed for SSA_1. In this case, the sodium introduced through NaHCO_3 was likely not sufficient to convert all PO_4^{3-} groups into highly soluble phases. This is supported by the observation that the crystalline phosphorus content is approximately 1–1.5 wt% lower than the recalculated total phosphorus content, which is consistent with the lower extraction efficiencies measured during leaching. Therefore, the difference in extraction efficiency does not appear to be related to NAC leaching effectiveness, as the extraction results correlate well with the mineralogical data. Instead, the limiting factor is likely the insufficient availability of sodium within the system to fully convert all phosphate phases into buchwaldite. It should be noted that the reaction system is highly complex, as sodium is not exclusively consumed by phosphate groups. As observed in the mineralogical analysis, sodium is also involved in the formation of other phases, such as thenardite, nepheline, albite, and lazurite, which incorporate both silicon and sulfur. Consequently, part of the available sodium is consumed by competing reactions, potentially limiting the complete transformation of phosphate phases. Under these conditions, a slight increase in the amount of NaHCO_3 could potentially favour a more complete conversion of phosphorus into highly soluble phases such as buchwaldite.

In the case of KHCO_3 , the increase in phosphorus solubility is slightly lower but still significant. For SSA_1, phosphorus extraction increased by approximately 34–44%, resulting in total extraction efficiencies of about 58–67%, with higher values again observed for the samples treated at 800 °C. For SSA_2, the increase ranged between 56–68%, corresponding to

extraction efficiencies of 76–88%, also showing slightly higher extraction for the treatment performed at 800 °C.

Although the absolute extraction values are lower compared to the NaHCO_3 system, the overall trend remains similar, with higher extraction observed for SSA_2 and for treatments performed at 800 °C. Even though quantitative phase analysis after thermochemical treatment could not be performed due to the lack of a suitable crystal structure for KCaPO_4 required for Rietveld refinement, the reaction mechanism appears to follow a comparable pathway.

The SSA_2 sample, characterised by a lower total phosphorus content, appears to undergo a more complete transformation into bioavailable phosphate phases such as KCaPO_4 under the same reagent dosage (30 wt% KHCO_3). However, the potassium-based reagent seems to be intrinsically less effective than NaHCO_3 for this specific application. This behaviour may be related to the chemical affinity of potassium within the system. As suggested by SEM–EDS and XRD analyses, potassium appears to preferentially associate with sulfur- and silicon-bearing phases rather than with phosphate species, in contrast to sodium, which more effectively participates in the formation of phosphate-bearing phases.

3.5.4.2 Formation and Leaching Behaviour of Hexavalent Chromium (Cr(VI)) in Treated Sewage Sludge Ash

Following the thermochemical treatment carried out in an air atmosphere on sewage sludge ash (SSA) samples, the formation of hexavalent chromium was observed. Cr(VI) quantification was performed using cuvette-based tests supported by spectrophotometric measurements.

The measured concentrations of hexavalent chromium ranged between 77 and 158 mg/kg, depending on the treatment temperature. Higher Cr(VI) concentrations were generally observed at higher treatment temperatures, reaching 126–158 mg/kg in samples treated at 1000 °C. No significant differences in Cr(VI) concentrations were observed between samples treated with sodium-based or potassium-based additives.

Total chromium concentrations were further evaluated by TXRF analysis following leaching in NAC. In this case, total chromium values were found to fall within a similar concentration range. These observations suggest that most of the chromium detected in solution is present in its hexavalent form. The formation of Cr(VI) can be attributed to the oxidation of trivalent chromium originally present in the SSA matrix, a process promoted by the high treatment temperatures and by the presence of Ca- and Na-containing compounds, as reported in previous

studies. In particular, sodium additives under oxidizing conditions may lead to the formation of chromate phases such as CaCrO_4 and Na_2CrO_4 [125].

Considering the use of KHCO_3 in the present work, the formation of analogous potassium-bearing chromate compounds during the thermochemical treatment is also likely.

The presence of Cr(VI) clearly limits the potential use of the treated materials for agricultural applications and highlights the need for possible mitigation strategies. Two potential approaches can be considered: conducting the thermochemical treatment under reducing conditions to prevent the oxidation of chromium or implementing a selective precipitation step to remove Cr(VI) from the NAC leachates.

3.6 Conclusions

Sewage sludge ash (SSA) is a complex, multiphase oxide system enriched in phosphorus and several macronutrients. The investigated samples contain significant concentrations of P (≈ 5.9 – 6.7 wt%) together with Ca, Mg, S, Na, and K. Compared with conventional phosphate rocks, SSA exhibits a markedly higher iron content (≈ 18 – 19 wt%), reflecting the extensive use of Fe-based salts during wastewater treatment and significantly influencing the mineralogical and particle distribution of phosphorus.

Phosphorus in the untreated ashes is hosted in multiple crystalline and amorphous phases with limited bioavailability. The main crystalline phase containing P is whitlockite, along with hydroxyapatite and tetra-potassium pyrophosphate, while a substantial aliquot of P is incorporated in the amorphous fraction, and in complex P–Si–Fe particles. Among these, partially backed particles and P–Si–Fe spheres have been found, exhibiting structures ranging from poorly crystalline to non-crystalline. This configuration strongly limits the efficiency of direct leaching processes, with both acids (see Chapter 2) and neutral ammonium citrate (NAC). In fact, the untreated SSAs exhibit very low phosphorus solubility in NAC. Only about 20% of the total phosphorus content was extracted from both SSAs, whereas other macronutrients, such as Ca, Na, and S, showed significantly higher solubility. These results confirm that the main limitation for the direct agronomic use of SSA is not the absence of nutrients, but the low bioavailability of phosphorus.

Microwave-assisted thermochemical treatment significantly modifies the mineralogical framework and phosphate-bearing phases of SSA. The treatment promotes partial melting and recrystallisation of the ash matrix, especially working with NaHCO_3 , transforming the original complex structures into a synthetic material composed mainly of high-temperature silicates, iron oxides, and newly formed phosphate phases.

NaHCO_3 proved to be the most effective additive for phosphorus transformation. The sodium-based treatment promotes the formation of buchwaldite (NaCaPO_4) as the dominant crystalline phosphate phase, indicating an extensive conversion of the original P-bearing phases, both in the crystalline and amorphous state. This transformation leads to a remarkable increase in phosphorus solubility, with extraction efficiencies reaching up to $\sim 100\%$ after NAC leaching. KHCO_3 shows a similar, albeit less efficient, effect. Although potassium-based treatment increases phosphorus solubility and promotes the formation of K–Ca phosphate phase (KCaPO_4), the conversion of the original phosphates remains incomplete, with residual whitlockite and hydroxyapatite persisting in the treated materials. Consequently, the overall

phosphorus extraction remains significantly lower than that achieved with NaHCO_3 . Although SEM observations suggest that the treatment at 800 °C leads to the formation of fewer K-bearing phosphate blebs, and therefore potentially lower amounts of KCaPO_4 , the final phosphorus concentrations measured after NAC leaching are higher for samples treated at this temperature. This observation suggests that additional conversion mechanisms may occur that do not involve a liquid-phase pathway followed by solidification, but instead proceed via solid-state reactions, forming potassium phosphate species that are soluble in NAC. These phases were not identified using the applied characterisation techniques, namely XRD-QPA and SEM-EDS.

Most heavy metals remain poorly soluble during leaching, despite their high total concentration in the ashes. Elements such as Ni, Cu, Zn, and Pb generally exhibit limited mobility in NAC, indicating that thermochemical treatment does not significantly alter their release into solution. However, a critical aspect of the process is the formation of hexavalent chromium (Cr(VI)) under high-temperature, oxidizing conditions, which poses a potential environmental constraint.

Overall, microwave-assisted thermochemical treatment combined with alkaline additives represents a promising strategy for phosphorus recovery from SSA. In particular, sodium-based activation enables an almost complete transformation of phosphorus into highly soluble phosphate phases. Nevertheless, further optimisation of the process is required to control the formation of Cr(VI) and to fully evaluate the potential reuse of the resulting ferro-siliceous solid residues.

Acknowledgments

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4. Lithium Iron Phosphate (LFP) Battery Crystal Structure Transformation by Microwave-Assisted Thermochemical Treatment and Simultaneous Phosphorus Recovery in Water

Following the investigation of sewage sludge ash, this chapter extends the materials-oriented approach to a different class of phosphorus-bearing secondary resources, namely lithium iron phosphate (LFP) battery black mass.

Although fundamentally different in origin, LFP shares with SSA the presence of phosphorus in structurally stable crystalline phases, where its extraction is hindered by strong chemical bonding. As previously discussed, understanding and controlling phase transformations is therefore essential to enable efficient resource recovery.

In this framework, microwave-assisted thermochemical treatment is explored not only as a strategy for lithium and phosphorus recovery in solution, but also as a tool to transform a low-value waste into potentially valuable phosphate-based materials. Particular attention is devoted to the identification of the crystalline phases formed during treatment, their stability, and their influence on the solubility of both lithium and phosphorus in subsequent water leaching processes.

Abstract

The rapid expansion of lithium iron phosphate (LFP) batteries in the stationary storage and electric mobility sectors has generated increasing concern regarding end-of-life management and resource security. While LFP chemistry offers significant advantages in terms of safety and durability, its growing diffusion poses strategic challenges related not only to lithium supply but also to the under-exploited recovery of phosphorus. In this context, the development of efficient, selective, and environmentally compatible recycling routes is essential to support circular-economy strategies and to reduce dependence on primary raw materials.

This study proposes a mild and potentially scalable thermochemical pathway for the dual recovery of lithium and phosphorus from spent LFP black mass. The approach combines microwave-assisted thermal treatment in the presence of sodium bicarbonate with a subsequent water-based leaching step, avoiding the use of strong mineral acids, oxidizing agents, or organic solvents.

During microwave treatment (600 °C, 20 min, air atmosphere), LiFePO_4 undergoes structural transformation through a sodium-assisted reaction pathway. The process promotes the formation of water-soluble lithium–sodium phosphate species and reactive lithium oxides, while iron is

preferentially stabilized in insoluble oxidic phases and Sodium Super Ionic Conductors (NASICON) structures. A subsequent room-temperature water leaching step allows the selective transfer of Li^+ and PO_4^{3-} into solution. The post-leaching solid residue is chemically stable and enriched in LiFeO_2 , NASICON structures and iron oxides, suggesting an additional valorisation pathway, for instance in catalytic or functional material applications. Therefore, the proposed protocol enables a dual-resource recovery strategy while generating a secondary solid fraction with potential added value. Overall, this work demonstrates that microwave-assisted sodium activation, coupled with mild aqueous extraction, represents a promising alternative to conventional hydrometallurgical routes for LFP recycling, aligning process simplicity, selectivity, and circular-economy principles.

Keywords: Lithium-Iron-Phosphate batteries, Lithium-Iron-Phosphate Black Mass, LFP, Lithium Ferrite, Olympite, Nalipoite, NASICON

4.1 Introduction

Lithium iron phosphate (LFP) batteries are a type of lithium-ion battery that utilizes lithium iron phosphate as the cathode material. LFP is a popular choice for cathode material in lithium-ion batteries due to its safety, relatively low cost, and exceptional cycle life [126]. LFP batteries also have a lower risk of thermal runaway compared to other cathode materials [127]. However, LFP batteries have some limitations. One disadvantage is their limited capacity compared to other cathode materials [128] [129]. In addition, cathodes exhibit poor electric conductivity and sluggish lithium-ion diffusion, which can affect their electrochemical performance [130]. The recycling of LFP batteries has been proposed through various methods, including hydrometallurgy, thermal treatment, mechanochemical processes, ion exchange, and adsorption. Hydrometallurgical processing is advantageous due to its low energy consumption and CO_2 emissions, and it allows for the recovery of high-purity Li [131]. Ion-exchange methods using strong and weak acid cation exchange resins have been explored for the recovery of Li from LFP materials [132]. Low-temperature thermal pretreatment has been used as an alternative method to dissociate the anode material from the LFP batteries, with minimal quality loss [133]. Acid-free mechanochemical processes have been able to selectively extract lithium from spent LFP battery cathode materials while reserving Fe in the form of FePO_4 [134]. In parallel, physical pre-treatment methods such as eddy current separation have been applied to separate non-ferrous metallic fractions from aluminum and LFP-containing mixtures, achieving reported separation efficiencies up to 100% [135].

However, the recycling process for LFP batteries faces several challenges and limitations. One major challenge is the low content of high-value metals, for example Co, which has resulted in little emphasis being placed on their recycling [136]. Additionally, the profitability and environmental performance of the proposed recycling processes, such as mechanical treatment followed by hydrometallurgical processing, are questionable [136], because several chemicals are mandatory for these processes. Overall, the challenges and limitations of the recycling process for LFP batteries include the low content of high-value metals, questionable profitability and environmental performance of current recycling methods, low-value elemental composition, waste management concerns, and the presence of hazardous materials.

Figure 52 shows the value of recycled electric vehicle batteries by typology, in 2020 (Statista. (June 28, 2021) [137]. In 2020, recycling NCM111 batteries proved to be the most profitable among electric vehicle battery types. Battery recycling operations could yield approximately \$42 per kilowatt-hour when processing NCM111 batteries. Conversely, LFP batteries had the lowest residual value, amounting to about \$15 per kilowatt-hour. In addition, considering that Cu and Al, originating from the anodic and cathodic foils, are separately recovered in the mechanical pre-treatment, the value attributed to the cathodic material is very limited for LFP batteries (4\$ per kilowatt-hour, with NCM111 having 32\$ per kilowatt-hour).

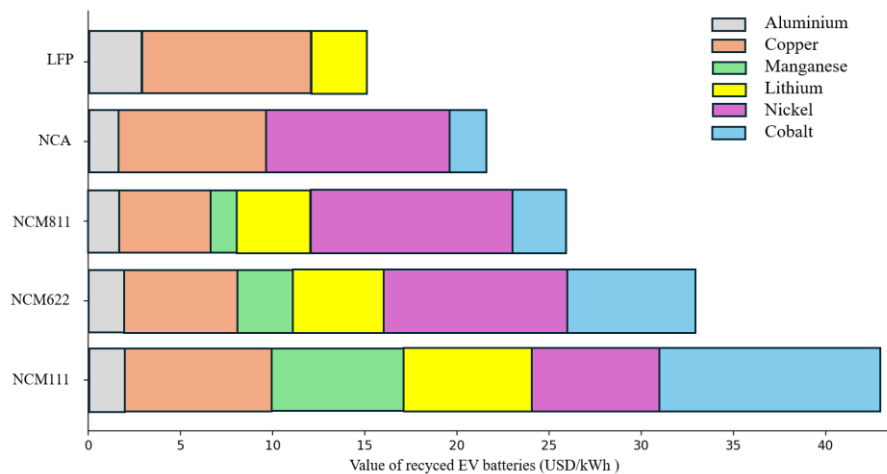


Figure 52. values of recycled electric vehicle (EV) batteries in 2020, by cathode chemistry (in U.S. dollars per kilowatt hour). NCM111 stands for nickel, cobalt and manganese batteries with Ni:Co:Mn ratio of 1:1:1) NCM622 with Ni:Co:Mn ratio of 6:2:2 and NMC811 with Ni:Co:Mn ratio of 8:1:1. NCA stands for lithium nickel cobalt aluminium oxides batteries. LFP strands for lithium-iron phosphate batteries

Moreover, the rapid proliferation of electric and hybrid vehicles employing LFP batteries has raised apprehensions regarding the waste issue when these batteries reach the end of their operational life [131].

In recent work, a new method based on a hybrid heating mechanism driven by microwave radiation to recover valuable raw materials from spent LIBs has been proposed. The system consists of an external silicon carbide susceptor and a graphite crucible containing the sample. This arrangement allows the carbothermic reduction of BM from spent LIBs in a few minutes with low power (ca. 1000 W) [138].

This work investigates the changes in the crystalline composition of lithium iron phosphate (LFP) batteries subjected to microwave-assisted thermochemical treatment in the presence of NaHCO_3 . Attention is devoted to identifying the crystalline phases in which phosphorus is redistributed after treatment, as well as those hosting lithium, another critical element of interest despite its relatively low concentration. Water leaching tests were subsequently performed to evaluate the solubility of the newly formed phases and to correlate phase composition with the leaching behaviour of Li and P. Unlike most previous studies, which primarily focus on elemental recovery efficiencies, this work adopts a materials-characterisation approach aimed at understanding how thermochemically induced phase transformations control the redistribution, speciation, and extractability of phosphorus and lithium.

Beyond its role in facilitating the recovery of critical elements, the microwave-assisted treatment is here proposed as a strategic approach for the valorisation of LFP black mass, which is typically considered a low-value waste stream due to the absence of high-value metals such as Co and Ni. Through controlled phase transformations, the process enables the conversion of the original LiFePO_4 structure into a range of new crystalline phases with distinct functional properties.

In particular, depending on the treatment conditions and reagent content, the formation of technologically relevant materials such as NASICON-type phosphates and sodium–lithium phosphate phases are observed. NASICON structures are of significant interest for their high ionic conductivity and potential application as solid electrolytes in sodium-ion and solid-state batteries [139] [140] [141] along with other lithium phosphate [142] [143] [144], while lithium ferrites [145] [146] [147] [148] phases may represent promising candidates for next-generation cathode or electrochemical materials.

This dual perspective—combining resource recovery with material transformation—positions microwave thermochemical treatment not only as a recycling strategy but also as a platform for the generation of advanced functional materials from waste. In this context, LFP black mass can be reinterpreted not merely as a secondary raw material for element recovery, but as a precursor for the synthesis of value-added compounds, thereby contributing to a more circular and sustainable approach to battery end-of-life management

4.2. Materials and methods

4.2.1 Samples, Reagents, and Preparation

The spent LFP battery sample was provided by Spirit s.r.l. (Chiampo, Vicenza, Italy) which performed pre-treatment on the black mass (BM) to remove the plastic component and separate the fractions characterised by a particle size of less than 400 μm (BM). The reagent employed for BM thermochemical treatment was NaHCO_3 (99.7% purity) by Chem-Lab NV. The BMs samples have been mixed with NaHCO_3 according to the following recipes:

- 70 wt% of BM and 30 wt% of NaHCO_3 (BM_R1)
- 50 wt% of BM and 50 wt% of NaHCO_3 (BM_R2)

The selected mass ratios were designed to evaluate the effect of increasing sodium availability on phase redistribution during microwave-assisted treatment, while also comparing the reactivity of two black masses with different initial compositions.

Each mixture was manually homogenized in an agate mortar to ensure intimate contact between solid reactants and to minimize compositional heterogeneity at the microscale. Subsequently, the blended powders were compacted into pellets (5 g each) using a hydraulic press under a maximum applied pressure of 300 bar.

4.2.2 Microwave Thermochemical Treatment.

The experiments were conducted using a PYRO Advanced Microwave Muffle Furnace (Milestone s.r.l., Bergamo, Italy). Treatments were performed under a controlled air flow of 45 $\text{m}^3 \text{h}^{-1}$, with a maximum self-adjusting microwave power of 1500 W. The temperature was set to 600 $^{\circ}\text{C}$, applying a heating rate of 50 $^{\circ}\text{C min}^{-1}$, followed by a 20 min isothermal holding stage.

4.2.3 Characterisation of Pre-Treated and MW-Treated Black Mass

4.2.3.1 X-ray Powder Diffraction and Quantitative Phase Analyses (XRPD-QPA)

The Black Mass before and after thermochemical treatment, and also after the leaching test, were characterised by X-ray diffraction (XRD) using an up-loading technique for sample preparation and acquiring it in a 2θ range of 10 $^{\circ}$ -90 $^{\circ}$. XRD analyses were carried out using an X'Pert Pro diffractometer (PANalytical, Malvern, UK) equipped with an X'Celerator detector and Cu anode (CuK α 1.5406 $\text{\AA}$) operating at 40 KV and 40 mA. Phase identification was performed using

HighScore Plus software (PANalytical). For the Rietveld refinement, Profex 5.2.0 was used to perform quantitative phase analysis (QPA) of the materials after each process step to establish relationships among the different Na-Li compounds and other crystalline phases for semiquantitative purposes. Alumina (≈ 10 wt%, Carlo Erba, CAS no. 1344-28-1) was used as an internal standard.

4.2.3.2 Scanning Electron Microscopy and Energy Dispersive X-ray Spectrometry (SEM-EDS)

The samples were analysed using two different scanning electron microscopes. The as-received materials were characterised using a FEI Quanta 400 FEG ESEM/EDAX Genesis X4M, operated in high-vacuum mode at 15 kV with a beam spot size of 4.5. Secondary electron (SE) imaging was used for surface topography, while the backscattered electron (BSE) mode was employed for phase identification. Semi-quantitative elemental analysis of selected regions was carried out via EDS microanalysis. Samples were analysed in the form of a polished block, prepared as described previously in Section SSA-1.

In contrast, the microwave-treated samples were examined using SNE-ALPHA, SEC Co., South Korea). The samples were fixed onto aluminium stubs with conductive carbon tape and coated with a thin gold layer to reduce surface charging during analysis. The instrument, featuring a spatial resolution of up to 5 nm and a maximum magnification of 250,000 $\times$, was operated at accelerating voltages between 1 and 30 kV. Micrographs were collected at various magnifications to assess particle morphology and surface features. For these materials, polished block preparation was not feasible, and analyses were therefore performed directly on powders. This approach was necessary due to the pronounced reactivity of the treated phases and their tendency to undergo deliquescence upon exposure to atmospheric moisture, requiring prompt post-treatment observation.

4.2.3.2 Acid digestion, Water Leaching, and Chemical Analysis of the Leachates

The as-received black masses were first subjected to acid digestion to determine their total elemental composition. Digestion was performed in aqua regia ($\text{HCl}:\text{HNO}_3 = 3:1$, v/v) at 80 °C under magnetic stirring for 6 h. After complete digestion, the resulting solutions were diluted with MilliQ water to a final volume of 25 mL before chemical analysis. These data were used as reference values for recovery calculations. The digested samples were quantitatively analysed by Total Reflection X-ray Fluorescence (TXRF) using a Horizon spectrometer (G.N.R., Italy). The instrument is equipped with a molybdenum X-ray tube coupled to a W/Si multilayer monochromator, generating a monochromatic Mo-K α excitation beam (17.44 keV). The fluorescence radiation emitted by the samples was detected using a 40 mm² silicon drift detector (SDD, KETEK GmbH) fitted with a 1 mm graphene window,

collimator, and protective polymer film. Measurements were performed in air at an operating voltage of 40 kV and a current of 15 mA. Gallium was employed as an internal standard for quantitative determination.

For comparison, the as-received materials were also leached directly in ultrapure MilliQ water under mild conditions, using a water-to-solid mass ratio of 50:1 (w/w) at room temperature under magnetic stirring (300 rpm) for 20 min.

The same aqueous extraction procedure was then applied to the microwave-treated mixtures. After leaching, the suspensions were vacuum-filtered, and both the solid residues and the corresponding liquid fractions were collected for subsequent characterisation and elemental quantification.

The leached samples were analysed through two different techniques. Ion chromatography (IC) with the Metrohm 883 Compact IC plus (Metrohm AG, Herisau, Switzerland) and a cation-exchange column, Metrosep C4-150/4.0 (Metrohm AG, Herisau, Switzerland), was used to determine the lithium (Li) content. The concentration of phosphorus (P) in the solution was measured using the Hach Lange DR 3800 spectrophotometer at the wavelength of maximum absorption (653 nm), with the ortho/total phosphate cuvette test LCK 348 (0.5 to 5.0 mg/l PO₄-P), also manufactured by Hach.

4.3. Results and discussion

4.3.1 Chemical, XRPD-QPA, and SEM-EDS of the as-collected Black Mass

The as-collected BM chemical composition is reported in Table 26. The major components, as reported, are Fe (≈ 22.4 wt%) and PO₄³⁻ (≈ 15.2 wt%), with a lower amount of Li detected at < 2 wt%. Other elements detected are aluminium (Al), copper (Cu), cobalt (Co) and nickel (Ni). These elements are present as impurities within the black mass (BM). Their occurrence may be attributed to the fact that LFP batteries are often processed in the same mechanical recycling facilities used to produce black masses derived from NCM batteries, leading to potential cross-contamination during the shredding and separation steps [149].

Table 16. Chemical analyses of BMI determined by IC (Li^+), ortho-phosphate cuvette test (PO_4^{3-}), and TXRF (*).

Element/Analyte	Black Mass (BM) LFP		
	Wt%		
Li^+	1.9	$\pm$	0.1
PO_4^{3-}	15.2	$\pm$	1.5
Fe^*	22.4	$\pm$	3.7
Al^*	1.6	$\pm$	0.5
Cu^*	0.2	$\pm$	0.1
Co^*	0.1	$\pm$	0.04
Ni^*	0.02	$\pm$	0.001

X-ray data are reported in Table 27, and the QPA plot in Figure 53. The BM consists mainly of graphite (C) and triphylite (LiFePO_4) characterised by an olivine-type structure [71]. Additional reflections indicate accessory phases arising from battery components, containing elements as Al and F. Berlinite (AlPO_4) originates from the aluminium current collector used on the cathode side to enhance electronic conductivity. Griceite (LiF) can be attributed to the solid electrolyte interphase (SEI) formed during battery cycling at the electrode–electrolyte interface, mainly resulting from the decomposition of the commonly used electrolyte salt LiPF_6 [150] [151]. Minor Co-bearing phases were also detected, with Cobalt Pyrophosphate ($\text{Co}_2\text{P}_2\text{O}_7$). These phases likely reflect cross-contamination during upstream mechanical pre-treatment.

Table 17. Quantitative Phase Analyses with the Rietveld method of BM. R_{wp} is the refinement agreement factor; χ^2 is the goodness-of-fit statistic from the Rietveld refinement.

Crystalline phase		Unit	BM
Name	Chemical formula		
triphylite	$LiFePO_4$		41.4 (8)
graphite	C		16.7 (2)
griceite	LiF		1.4 (2)
berlinite	$AlPO_4$	Wt%	1.6 (2)
Co-Pyrophosphate	$Co_2P_2O_7$		3.5 (2)
amorphous			35.4 (26)
Cr. Phosphorus	P		10.48
R_{wp}			1.50
χ^2			2.21

The total crystalline P quantified by QPA is 10.48 wt%, coming mainly from triphylite but also from Co-pyrophosphate and berlinite. The total P quantified by this technique provides additional information beyond the PO₄³⁻ from chemical analyses about the actual P content of the BM. In addition, the QPA provides information about the amorphous content, quantified at $\approx$ 33 wt%. Most likely, the amorphous is composed mainly of graphite, considering that the graphite from spent LIBs usually exhibits severe surface damage [149], as an increased interlayer spacing of graphite layers in comparison to the virgin material, and the presence of amorphous carbon species.

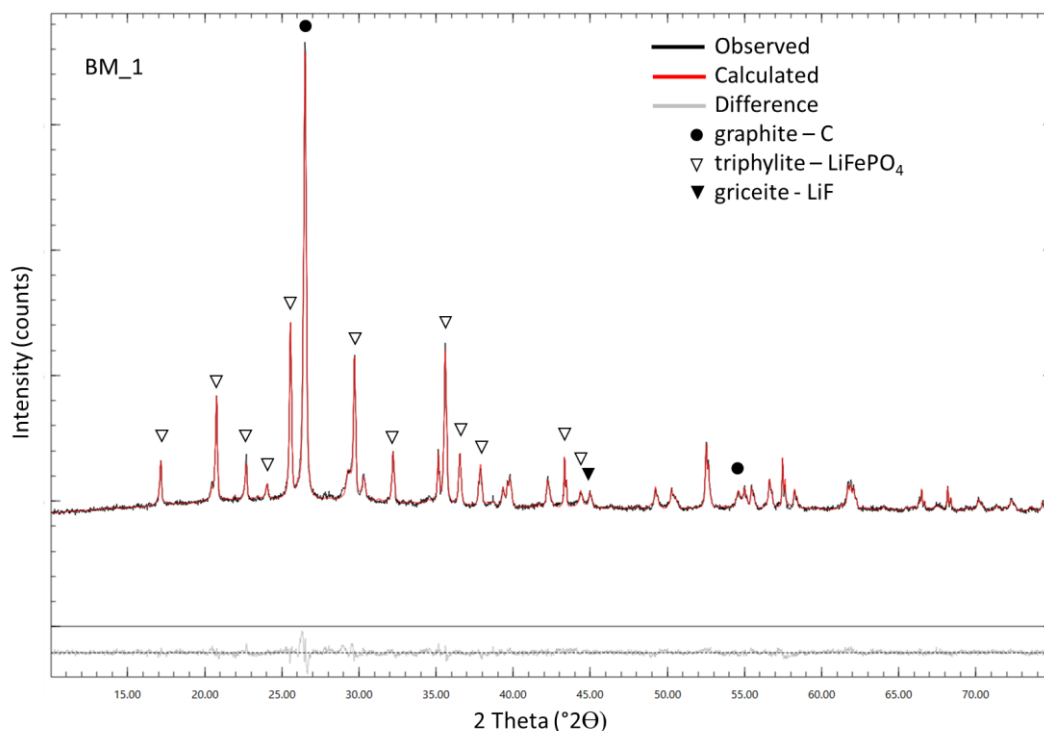


Figure 38. Rietveld refinement plot of BM_R1 treated at 600 °C for 20 minutes

SEM-EDS data shown in Figures 54 and Table 28 provide very interesting information about the particles composing the BM sample. The particles exhibit a wide size distribution (Figure 54), as the sample consists of black mass with a particle size below 400 μm . Two main particle types can be identified.

The first type consists of light-coloured particles with a predominantly rectangular morphology and fractured surfaces resulting from mechanical grinding (Figure 54A–E). These particles correspond to the cathodic component of the material. EDS spectra (Z1 and Z2 in Figure 54B) indicate that the main elements present are O, P, and Fe, while lithium cannot be detected with this analytical technique. These particles can therefore be attributed to triphylite (LiFePO_4), representing the cathode material of the battery.

At higher magnification (Figure 54C), the cathodic particles appear to consist of regions with different contrast, mainly grey and white areas. EDS analyses revealed local variations in the relative intensities of Fe and P among these regions. The grey areas exhibited comparatively higher P signals (EDS spectrum Z4), whereas the lighter regions showed relatively higher Fe signals (EDS spectra Z5 and Z8, Figure 54E). In addition, some areas displayed a more balanced Fe/P ratio (EDS spectrum Z7, Figure 54E). These observations indicate a certain degree of particle-scale heterogeneity within the cathodic material. Such variations may arise from the complex nature of industrial black mass particles, which can consist of agglomerated fragments, partially altered domains, and surface

topography effects influencing the EDS interaction volume. Therefore, the observed Fe/P variations should not be interpreted as direct evidence of compositional zoning within individual LiFePO₄ crystals.

The second particle type consists of darker particles with black coloration and morphologies ranging from irregular to spherical. EDS spectra (Z3 in Figure 54B and Z9 in Figure 54F) indicate that these particles are mainly composed of carbon, and they can therefore be attributed to graphite originating from the anode material.

Finally, a small number of particles containing additional elements were detected, likely resulting from contamination. For instance, the particle analysed in Figure 54D (EDS spectrum Z6) shows the presence of S and Cu, while the particle analysed in Figure 54F (EDS spectrum Z10) contains Mn and Co.

Table 28. EDS semiquantitative analysis of BM reporting the main particle of LFP cathodic and anodic material, and those present from cross-contamination.

Black Mass										
Element	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9	Z10
Wt%										
C	24.6	25.5	100.0	11.2	17.0	7.7	13.0	11.4	100.0	5.9
O	22.6	22.2	-	33.6	23.6	1.8	32.3	29.8	-	5.1
P	18.0	17.8	-	28.9	21.2	0.5	27.0	21.5	-	-
Fe	34.7	34.4	-	26.3	38.3	2.2	27.7	37.2	-	-
Mn	-	-	-	-	-	-	-	-	-	24.4
Co	-	-	-	-	-	-	-	-	-	32.6
Ni	-	-	-	-	-	-	-	-	-	32.1
Cu	-	-	-	-	-	70.6	-	-	-	-
S	-	-	-	-	-	17.2	-	-	-	-

These results highlight that, even when derived from a single battery chemistry, black mass can exhibit significant heterogeneity in both composition and impurity content. While many recycling approaches rely on intensive pre-treatment steps to isolate a relatively pure LiFePO₄ cathode fraction and optimize downstream recovery, the present study deliberately considers an impurity-rich black mass that includes current-collector fragments, binder residues, and trace metallic elements. This

approach reduces the need for complex pre-treatment operations, thereby improving process sustainability, and provides a more realistic assessment of whether such impurities may hinder the recovery of lithium and phosphorus under mild processing conditions.

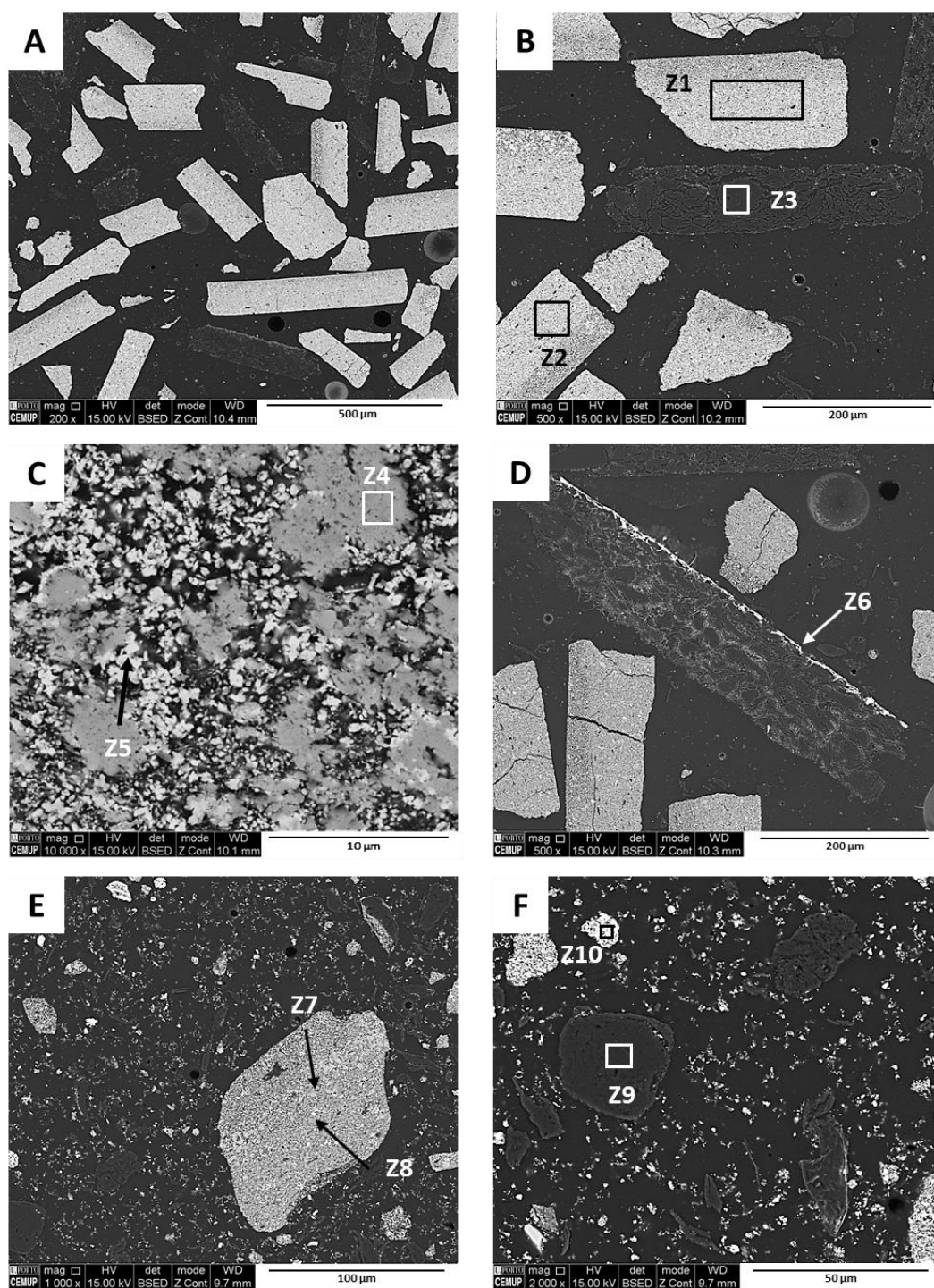


Figure 394. SEM-EDS analysis of as-collected Black Mass: A) low magnification with big grains of LiFePO_4 and graphite (sample BM; BSE mode; 200x); B) higher magnification BM, spectra Z1, Z2 and Z3 (sample

BM; BSE mode; 500x); C) high magnification LiFePO_4 grain, contrast in grayscale is associated with variations in local composition (sample BM; BSE mode, 10000x); D) wide graphite grain with a layer of CuS , spectrum Z6 (sample BM; BSE mode, 500x); E) high magnification of the smallest particles showing submicrometric particles, spectra Z7 and Z8 (BM; BSE mode, 1000x); F) high magnification of the smallest particles showing spherical graphite poorly crystalline, and a particle of Ni-Mn-Co oxide, spectra Z9 and Z10 (BM; BSE mode; 2000x).

4.3.2 Microwave Thermochemical Treatment and Crystalline Phase Transformation

The BM treated according to the recipes BM_R1 (70-30) and BM_R2 (50-50) were microwave-treated at 600 °C for 20 min, resulting in weight losses of about 37% and 45%, respectively. The tablets were ground and analysed by XRD-QPA (Figures 55 and 56 and Table 29) to assess structural changes. The diffraction patterns clearly show that the cathode active material LiFePO_4 , originally present in BM, is no longer detectable after treatment, indicating complete phase transformation under microwave conditions. Graphite is still observed, although in reduced amounts, especially in BM_R2 (< 1 wt%), confirming partial carbon consumption during the process. The use of different reagent amounts resulted in the formation of two distinctly different crystalline products, both in terms of identified and quantified phases. The only phases common to both samples are dilithium peroxide (Li_2O_2), present as a minor phase (< 4 wt%), and iron oxides, whose speciation strongly depends on the treatment conditions.

In BM_R1, iron is predominantly present as hematite (Fe_2O_3 , ≈ 16 wt%), with a minor contribution of magnetite (Fe_3O_4 , ≈ 1 wt%). In contrast, BM_R2 is mainly characterised by magnetic iron oxides, with magnetite (≈ 3 wt%) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$, ≈ 11.6 wt%) as the dominant phases, while hematite is present only in a limited amount (≈ 2.0 wt%). These results indicate that a higher reagent content promotes the transformation of iron into magnetic oxide phases. This behaviour can be associated with changes in the local redox conditions induced by the increased availability of sodium species and the decomposition of NaHCO_3 during microwave heating, which may favour partial reduction and subsequent reorganization of iron into spinel-type structures such as magnetite and maghemite, rather than the formation of fully oxidized hematite.

Table 29. QPA analysis of the MW-treated BM according to recipe 1 and recipe 2.

Crystalline phase		Unit	BM_R1	BM_R2
Name	Chemical formula			
nalipoite	NaLi ₂ PO ₄		10.6 (4)	-
olympite	LiNa ₅ (PO ₄) ₂		-	40.6 (11)
Na3-Fe2-Pphosphate	Na ₃ Fe ₂ (PO ₄) ₃		12.4 (8)	-
Na4-Fe2-phosphate	Na ₄ Fe ₂ (PO ₄) ₃		5.1 (3)	-
graphite	C		3.8 (2)	0.8 (1)
dilithium peroxide	Li ₂ O ₂		2.3 (2)	4.1 (6)
β-lithium metaphosphate	β-Li ₃ PO ₄		12.1 (5)	-
lithium ferrite	Li _{1.05} Fe _{0.95} O ₂	Wt%	-	8.1 (2)
lithium ferrite	LiFe ₅ O ₈		1.9 (1)	-
hematite	Fe ₂ O ₃		15.8 (9)	1.9 (1)
maghemite	γ-Fe ₂ O ₃		1.1 (2)	14.4 (3)
villiaumite	NaF		-	1.5 (1)
chiolite	Na ₅ Al ₃ F ₁₄		-	1.2 (2)
amorphous			34.9 (14)	27.4 (7)
Cr. Phosphorus	P		9.77	10.48
R _{wp}			1.88	1.46
χ ²			2.30	1.58

A more detailed analysis of the individual samples highlights significant differences in phase complexity. BM_R1 is characterised by a highly heterogeneous crystalline assemblage, indicating the formation of a complex product that may also complicate subsequent leaching processes. The main Li- and P-bearing phases identified include nalipoite (NaLi₂PO₄, ≈ 11 wt%), together with two sodium–iron phosphates, Na₃Fe₂(PO₄)₃ (≈ 13 wt%) and Na₄Fe₂(PO₄)₃ (≈ 5 wt%). Lithium ferrite (LiFe₅O₈) is also detected, although in minor amounts, along with β-Li₃PO₄ (≈ 12 wt%). The total crystalline phosphorus content is ≈ 9.77 wt%.

Overall, lithium and phosphorus are distributed among multiple crystalline phases with different chemical environments, most of which are expected to be poorly soluble in water, except for Li₂O₂. The amorphous fraction is relatively high (≈ 34.9 wt%) and may consist of residual graphite, amorphous phosphate species, or poorly crystalline iron oxides not detectable by XRD.

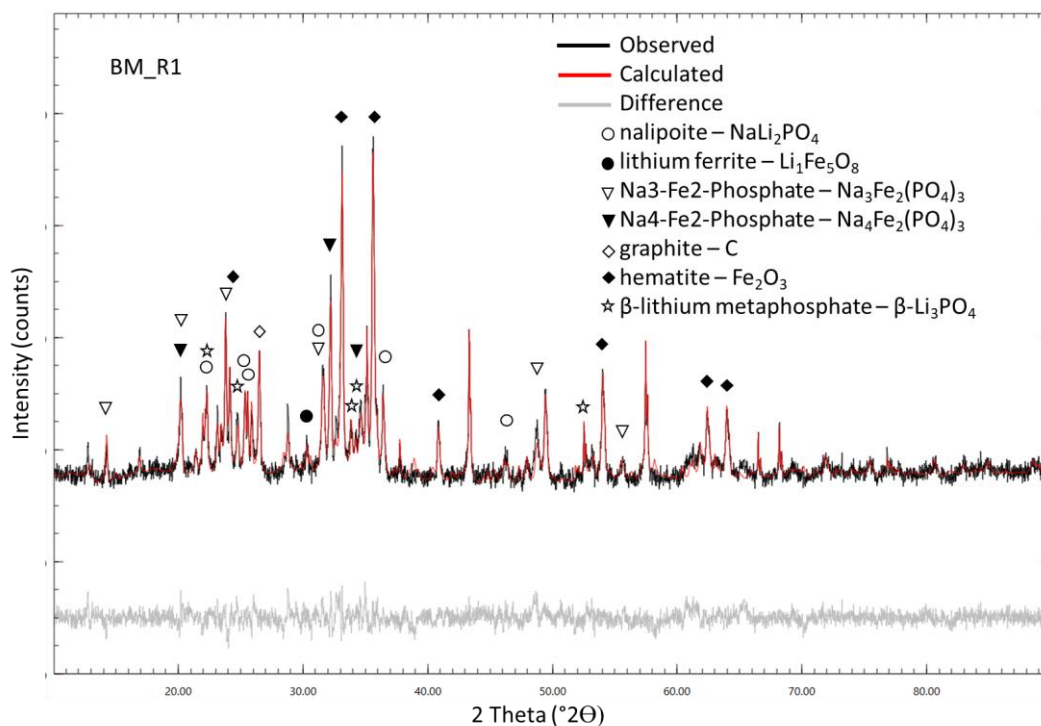


Figure 405. Rietveld refinement plot of BM_R1 treated at 600 °C for 20 minutes

In contrast, BM_R2 exhibits a significantly simpler crystalline composition. The mineralogy is dominated by a single sodium–lithium phosphate phase, olympite ($\text{NaLi}_5(\text{PO}_4)_2$, ≈ 41 wt%), and no additional crystalline phosphate phases are detected. The total crystalline phosphorus content is slightly higher (≈ 10.48 wt%). Lithium is mainly hosted in olympite but also occurs in lithium ferrite ($\text{Li}_{1.05}\text{Fe}_{0.95}\text{O}_2$) in appreciable amounts (≈ 8 wt%). Minor sodium–fluorine phases, such as villiaumite (NaF) and chiolite ($\text{Na}_5\text{Al}_3\text{F}_{14}$), are also present, each below 2 wt%. The amorphous fraction is lower than in BM_R1, accounting for ≈ 27 wt%.

These results clearly indicate that increasing the reagent content leads to the formation of a simpler, more homogeneous crystalline system, in which lithium and phosphorus are concentrated into fewer, more well-defined phases, potentially enhancing their reactivity during subsequent leaching. An interesting aspect is that all treatments led to the formation of structurally relevant compounds. BM_R1 contains two phases belonging to the NASICON family (Na Super Ionic CONductors), namely $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ and $\text{Na}_4\text{Fe}_2(\text{PO}_4)_3$ [152] [153] [154]. These materials are characterised by an open three-dimensional framework built from corner-sharing MO_6 (FeO_6 as in this scenario) octahedra and PO_4 tetrahedra, which enables high ionic conductivity, especially for Na^+ ions. For this reason, NASICON-type compounds have been extensively studied for applications in solid-state batteries and electrochemical devices [155] [156] [157].

However, despite their structural interest, these phases are expected to be relatively stable and poorly soluble in water under mild conditions. Their robust framework, which facilitates ionic transport in

the solid state, also confers high chemical stability and resistance to dissolution. As a result, incorporating phosphorus into NASICON-type structures may hinder its release during water leaching. This represents a drawback of the lower-reagent formulation (BM_R1), where phosphorus is distributed among multiple stable crystalline phases, including NASICON-type compounds. In contrast, higher reagent contents favour the formation of simpler and more reactive sodium–lithium phosphate phases, thereby enhancing phosphorus and lithium recovery.

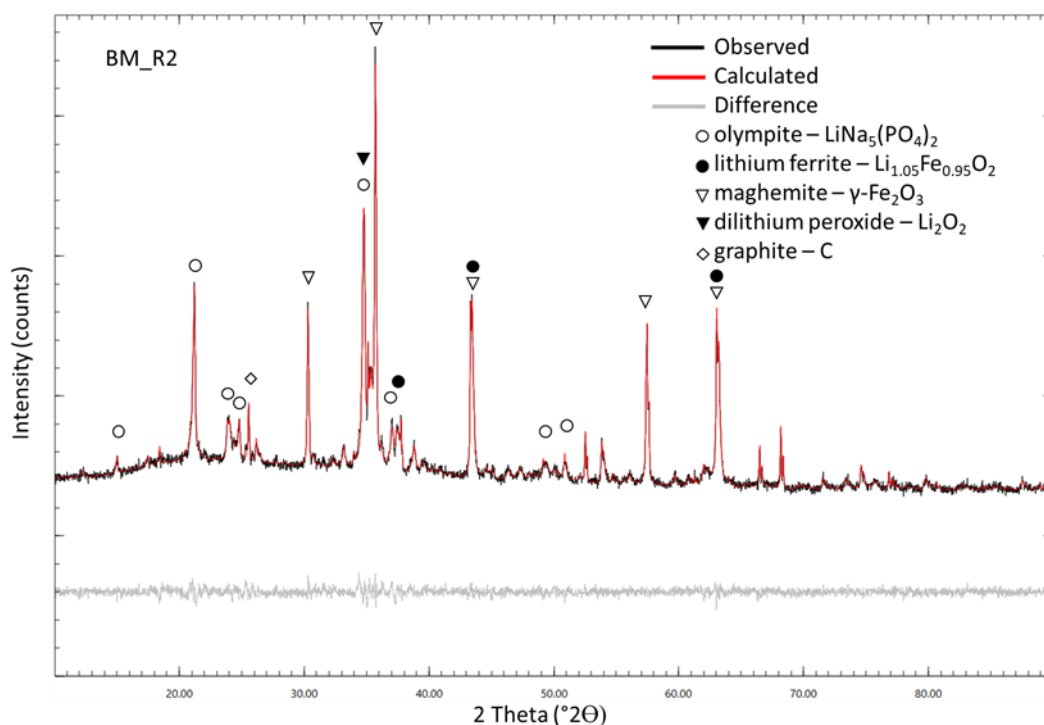


Figure 416. Rietveld refinement plot of BM_R2 treated at 600 °C for 20 minutes

BM_R2 is characterised by the formation of one of the most water-soluble phosphate phases reported in the literature, namely olypite ($\text{NaLi}_5(\text{PO}_4)_2$). In this case, lithium and phosphorus are predominantly incorporated into a single crystalline phase that is expected to be readily dissolved during water leaching, thus promoting their efficient transfer into the aqueous phase.

In addition, the formation of lithium ferrite ($\text{Li}_{1.05}\text{Fe}_{0.95}\text{O}_2$) is observed. Notably, the only available crystal structure currently suitable for Rietveld refinement corresponds to entry 1541312 in the COD database [158], which was therefore adopted for phase identification and quantification. The formation of this lithium ferrite in the treated samples can be rationalized considering its structural relationship with iron oxides, particularly maghemite ($\gamma\text{-Fe}_2\text{O}_3$). Maghemite is a defect spinel characterised by cation vacancies within an iron oxide framework, which makes it structurally predisposed to accommodate lithium ions.

Previous studies have shown that lithium insertion into defect spinel structures, such as $\gamma\text{-Fe}_2\text{O}_3$, proceeds through the progressive occupation of octahedral sites, accompanied by the migration of Fe cations and a structural rearrangement toward a rock-salt-type phase. Lithium incorporation drives a transformation from the spinel structure to a disordered rock-salt configuration, in which both Li^+ and Fe^{3+} occupy octahedral positions within a cubic lattice. In this context, the formation of lithium ferrite can be interpreted as the final stage of this structural evolution, in which lithium is fully incorporated into the iron oxide framework, yielding a rock-salt-type lithium ferrite. The availability of a disordered cubic phase, as reported in early studies on lithium ferrite, further supports this mechanism, as it represents a stable configuration resulting from cation redistribution and ordering/disordering processes at elevated temperature. Therefore, in the present system, the coexistence of maghemite and LiFeO_2 suggests that microwave thermochemical treatment promotes lithium diffusion into iron oxide domains, thereby inducing a spinel-to-rock salt transformation pathway. This process is likely facilitated by the high defect concentration of $\gamma\text{-Fe}_2\text{O}_3$ and the rapid heating conditions, which enhance cation mobility and favour the formation of lithium ferrite as a thermodynamically stable phase [159] [158].

Based on the mechanisms discussed above, the formation of LiFeO_2 -rich residues is particularly interesting, as LiFeO_2 has been identified as a potentially active catalytic phase, thereby offering a promising route for direct residue valorisation without the need for extensive downstream processing [160].

In this case, SEM–EDS analyses are of limited effectiveness for the characterisation of the synthesized samples, primarily due to the inability of the technique to detect lithium. While in the as-received black mass it is relatively straightforward to identify P- and Fe-rich particles as belonging to the cathodic fraction, this distinction becomes significantly more challenging after high-temperature treatment (600 °C). Following synthesis, the formation of multiple new phases, often with similar elemental compositions but different crystal structures, requires a more precise phase discrimination that cannot be reliably achieved by SEM–EDS alone. As a result, the technique becomes less suitable for providing unambiguous compositional and structural information, particularly for the more complex sample BM_R1. For this reason, SEM analyses were selectively reported only for BM_R2, which exhibits a simpler crystalline assemblage and is therefore more suitable for meaningful microstructural interpretation. Figure 57 shows a representative SEM micrograph of the treated sample, highlighting particles attributed to ol ympite with sizes below 30 μm . These grains exhibit an irregular, sub-angular morphology with relatively rough surfaces, indicative of crystallisation and partial sintering during the thermal treatment. EDS point analyses (Table 30) confirm that regions Z1 and Z4 correspond to Na–P-rich phases, consistent with ol ympite

composition. In contrast, other areas of the same particles (Z2 and Z3) display a different surface contrast and are enriched in iron and oxygen, indicating the presence of iron oxide layers. These observations suggest that some ol ympite grains are partially coated or decorated with iron oxide phases, likely formed during the redistribution and oxidation of iron under microwave-treatment conditions.

Table 30. EDS semiquantitative phase analyses of sample BM_R2.

BM_R2				
Element	Z1	Z2	Z3	Z4
Wt%				
O	57.3	61.3	60.7	55.1
Na	33.1	6.5	6.8	33.1
P	9.4	0.7	1.0	11.2
Fe	0.2	31.5	31.6	0.6

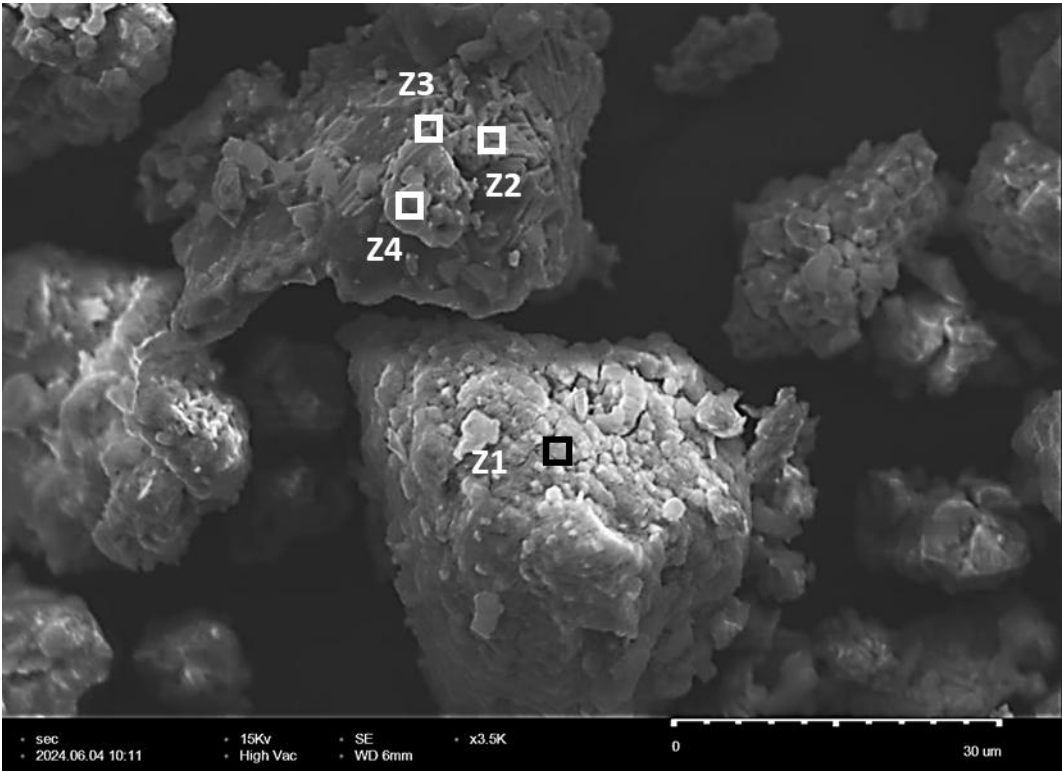


Figure 57. SEM-EDS analysis of BM_R2 showing grains of ol ympite (spectra Z1 and Z4) partially covered by Fe-oxides (particles corresponding to EDS zone Z2 and Z3) (SE mode, 3500 x)

4.3.3 Lithium and Phosphate Solubility and Analysis of the Solid Residues

Leaching tests were performed on both the as-collected black mass and the microwave-treated samples. As shown in Table 31, the untreated black mass releases only negligible amounts of lithium and phosphate into the aqueous phase. In contrast, microwave treatment promotes the formation of new compounds, including both water-soluble and water-insoluble phases. Leachates derived from BM_R1 and BM_R2 were analysed by ion chromatography (Li^+) and orthophosphate colorimetric methods (PO_4^{3-}), and the results are reported in Table 31. The results indicate that both lithium and phosphate are effectively transferred into the aqueous phase after treatment, with a strong dependence on NaHCO_3 content. In all cases, the extracted amounts are significantly higher than those obtained from the untreated black mass. For BM_R1, the lithium concentration in solution is 0.25 wt%, while phosphate reaches 2.21 wt%. These values increase substantially for BM_R2, where lithium and phosphate concentrations reach 0.85 wt% and ≈ 13.4 wt%, respectively.

Table 181. Chemical analyses of leachates for the untreated BM, BM_R1 and BM_R2.

Analyte	Leach BM	Leach BM_R1	Leach BM_R2
	Wt%		
Li^+	0.006 ± 0.0001	0.25 ± 0.02	0.85 ± 0.07
PO_4^{3-}	0.011 ± 0.001	2.21 ± 0.15	13.37 ± 1.23

These trends are consistent with the phase evolution observed by XRD. The higher NaHCO_3 content in BM_R2 promotes the formation of ol ympite and reduces the presence of less reactive secondary phases. XRD analysis of the solid residue after leaching (BM_R2_SR, Figure 58) shows that only iron oxides (maghemite, magnetite, hematite), graphite, and lithium ferrite remain, indicating that P-bearing crystalline phases have been effectively dissolved.

In contrast, the XRD pattern of the BM_R1 residue (BM_R1_SR, Figure 58) still shows the presence of all major Li- and P-bearing phases, including nalipoite, lithium ferrite, NASICON-type phosphates, and $\beta\text{-Li}_3\text{PO}_4$, confirming their limited solubility under the adopted conditions.

The quantitative phase analysis of solid residues (Table 32) was performed without an internal standard; therefore, no information on the amorphous content could be obtained, and the relative amounts of the crystalline phases are likely overestimated.

Overall, these results demonstrate that the combination of microwave treatment and NaHCO_3 effectively disrupts the original LiFePO_4 structure, promoting the formation of new lithium-, iron-, and phosphate-bearing crystalline phases. However, the nature and leachability of the reaction products strongly depend on the NaHCO_3 dosage. In the BM_R2 formulation, the transformation of LiFePO_4 resulted in the formation of phosphate phases that were highly soluble in water, whereas the newly formed Li- and Fe-bearing compounds remained largely insoluble. Consequently, phosphorus could be selectively transferred to the aqueous phase while iron-rich phases were retained in the solid residue. In contrast, the BM_R1 formulation produced reaction products that were predominantly water-insoluble, resulting in the retention of a significant fraction of both phosphorus and lithium within the treated matrix after processing at 600 °C. These findings indicate that a sufficient NaHCO_3 dosage is required not only to destabilize the LiFePO_4 structure but also to promote the formation of highly water-leachable phosphate species.

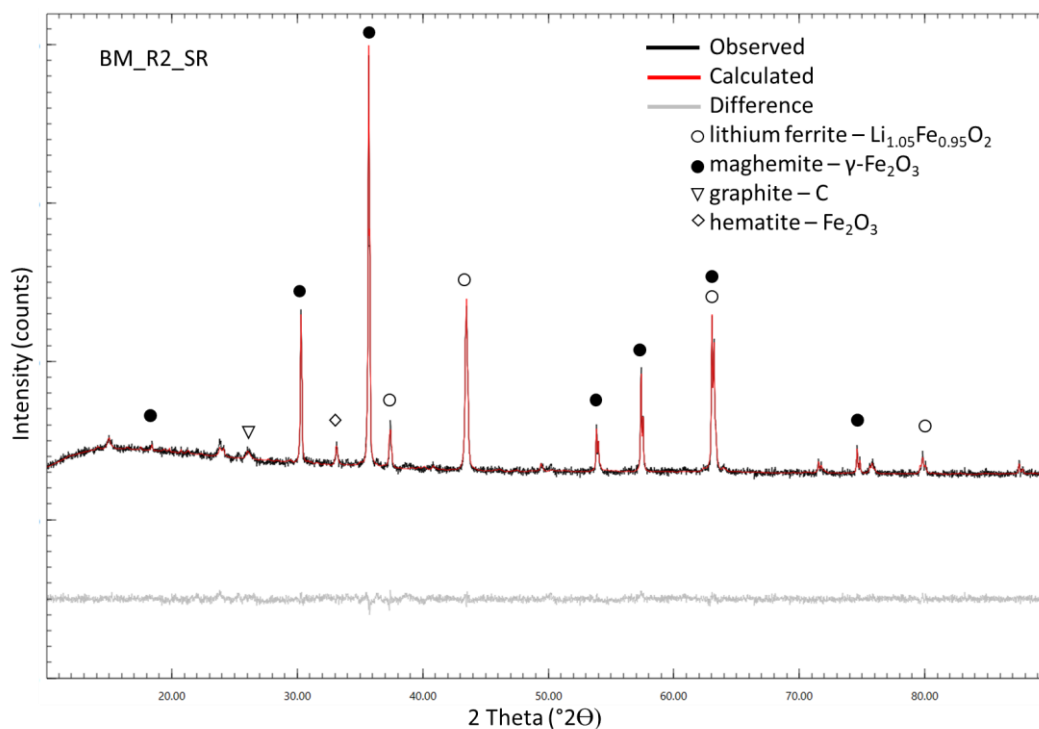


Figure 58. Rietveld refinement plot of BM_R2_SR after water leaching

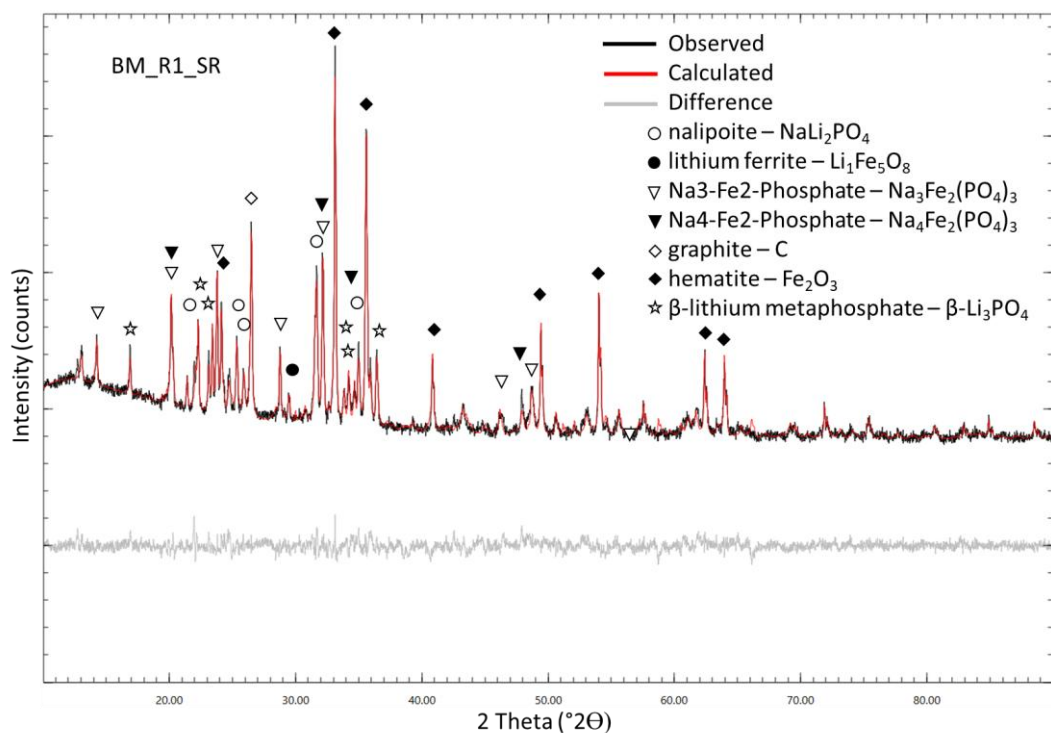


Figure 59. Rietveld refinement plot of BM_R1_SR after water leaching

Table 32. Quantitative Phase Analysis without an internal standard of the solid residue after the water-leaching test.

Crystalline phase		Unit	BM_R1_SR	BM_R2_SR
Name	Chemical formula			
Nalipoite	NaLi_2PO_4		16.0 (4)	-
Na3-Fe2-Phosphate	$\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$		23.6 (9)	-
Na4-Fe2-Phosphate	$\text{Na}_4\text{Fe}_2(\text{PO}_4)_3$		8.8 (3)	-
Graphite	C		5.3 (4)	2.5 (2)
β-lithium metaphosphate	$\beta\text{-Li}_3\text{PO}_4$		17.8 (3)	-
Lithium Ferrite	$\text{Li}_{1.05}\text{Fe}_{0.95}\text{O}_2$		-	41.6 (12)
Lithium Ferrite	LiFe_5O_8		3.2 (2)	-
Hematite	Fe_2O_3		23.4 (7)	5.4 (4)
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$		1.9 (1)	50.4 (15)
R_{wp}			1.88	1.46
χ^2			2.30	1.58

4.4 Conclusions

The characterisation of the LFP black mass clarified its crystalline structure, which is predominantly composed of the cathodic phase triphylite (LiFePO_4) and the anodic phase graphite (C), with a total crystalline phosphorus content of ≈ 10.5 wt%. Quantitative phase analysis (QPA) also revealed the presence of secondary crystalline phases, partly related to battery chemistry (e.g., griceite) and partly to contamination, such as cobalt pyrophosphate and berlinite, although in minor amounts. Chemical analysis further confirmed a high phosphate content, while lithium was found to be present in relatively low amounts (<2 wt%), making these materials particularly attractive for phosphorus recovery. SEM observations showed a heterogeneous particle morphology, with prismatic, fractured particles in the coarser fraction and more rounded, sub-spherical particles in the finer fraction.

Microwave-assisted thermochemical treatment in the presence of sodium bicarbonate (600°C , 20 min, air) promotes a complete transformation of the original LiFePO_4 cathode into new crystalline phases. In the case of BM_R1, treated with a lower amount of reagent, a complex assemblage of phases is formed, including NASICON-type structures and $\beta\text{-Li}_3\text{PO}_4$, which are of interest as solid electrolyte materials. In contrast, the higher NaHCO_3 content used for BM_R2 leads to the formation of a simpler phase assemblage, dominated by a sodium–lithium phosphate phase (olympite), together with lithium ferrite (LiFeO_2) and iron oxides, predominantly in magnetic forms.

Subsequent water leaching at room temperature (20 min) enables the selective transfer of Li^+ and PO_4^{3-} into the aqueous phase. A significant improvement in recovery is observed only for BM_R2 (50 wt% NaHCO_3). XRD analysis of the corresponding solid residues (BM_R1_SR and BM_R2_SR) confirms that, due to the low solubility of the phases formed in BM_R1, most of the crystalline Li- and P-bearing phases remain in the residue after leaching. In contrast, BM_R2_SR shows the absence of crystalline phosphate phases after leaching, with the residue mainly composed of iron oxides (maghemite and hematite), lithium ferrite, and residual graphite. This indicates that the majority of phosphorus has been successfully transferred into the aqueous phase.

Overall, these results demonstrate that treatment with a higher reagent content leads to a simpler and more favourable phase assemblage, enabling efficient phosphorus transfer into solution while leaving a solid residue that could potentially be further valorised. In particular, the residue, rich in magnetic iron oxides and lithium ferrite, may be suitable for magnetic separation, although the coexistence of these phases could limit separation efficiency. In contrast, the BM_R1 treatment results in the formation of structurally interesting compounds, particularly NASICON-type phases, which are potentially valuable for solid-state electrochemical applications but difficult to manage due to their chemical stability and the heterogeneous nature of the resulting powder. Future work could focus on

optimizing the thermal treatment conditions to selectively promote the formation of these functional materials starting from LFP battery waste.

This work demonstrates that LFP battery waste can be strategically transformed either into a source of recoverable phosphorus or into functional advanced materials, highlighting the potential of microwave-assisted processing as a versatile platform for the sustainable and selective valorisation of critical resources.

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5. Final Remarks and Future Perspectives

5.1 Final Remarks

This thesis investigated the role of crystalline phase transformations in controlling phosphorus recovery from secondary inorganic resources. The scope was to understand how the mineralogical evolution of phosphorus-bearing phases affects their reactivity, solubility, and recovery potential. Two different secondary resources were studied: sewage sludge ash (SSA) and black mass derived from spent lithium iron phosphate (LFP) batteries.

Chapter 2 of the work focused on CO₂ absorption by SSA as a potential pretreatment for phosphorus recovery. The carbonation process promoted the formation of carbonate phases and reduced the pH of the ash suspension without significant improvement in phosphorus extraction. Moreover, the results demonstrate that the recovery of phosphorus from SSA cannot be effectively enhanced through pH modification alone, as the stability of the phosphorus-bearing crystalline phases remains the dominant factor controlling leaching behaviour.

Chapter 3 of the work investigated microwave-assisted thermochemical treatments of SSA in the presence of 25 wt% of NaHCO₃ and KHCO₃ at two different temperatures (800 °C and 1000 °C). The treatments successfully promoted the transformation of poorly soluble phosphate into new crystalline phases, including NaCaPO₄, buchwaldite, and KCaPO₄. These phase transformations significantly increased phosphorus extractability by leaching with Neutral Ammonium Citrate (NAC) up to 99% and demonstrated the importance of controlling mineralogical evolution during treatment. The results confirmed that thermochemical processing, especially with Na-based reagents, represents a promising route for converting crystalline and amorphous P-bearing phases into more bioavailable crystals.

Chapter 4 of the work addressed the valorisation of LFP black mass through microwave-assisted thermochemical treatment with NaHCO₃. The treatment disrupted the cathodic LiFePO₄ crystal structure and promoted the formation of new lithium-, iron-, and phosphate-bearing phases. The water leaching experiments demonstrated that phosphorus and lithium recovery strongly depend on the nature of the newly formed crystalline phases. Higher NaHCO₃ additions favoured the formation of a highly water-soluble phosphate identified as ol ympite, significantly improving the recovery of both elements (Li and P). In contrast, the use of a lower NaHCO₃ dosage promotes the formation of water-insoluble crystalline phases such as nalipoite and NASICON structures. These findings highlight the potential of phase transformation engineering as a tool for the recovery of critical raw materials from LFP battery waste.

Overall, the results of this thesis demonstrate that phosphorus recovery is governed not only by chemical composition but also by the crystalline structure of the host phases. The ability to control phase transformations therefore represents a key strategy for designing more effective recovery processes from complex secondary resources.

5.2 Future Perspectives

Regarding the carbonation of SSA, the obtained results suggest limited potential for future development as a standalone strategy for phosphorus recovery. Although CO₂ sequestration effectively promotes pH reduction, it does not substantially alter the stability of the phosphorus-bearing crystalline phases when combined with H₂SO₄ 0.2 M. Consequently, future research efforts are likely to be more effectively directed toward technologies capable of directly modifying phase composition and crystal structure or focusing only on CO₂ capture.

In contrast, the microwave-assisted thermochemical treatment of SSA presents several promising research opportunities. Future work should primarily focus on eliminating Cr(VI) formation while maintaining high phosphorus conversion and recovery efficiencies. Once this target has been achieved, the process could be benchmarked against alternative phosphorus recovery technologies through techno-economic and thermodynamic assessments. These studies will be essential to evaluate the industrial feasibility and competitiveness of the proposed process.

The treatment of LFP black mass represents a particularly promising research field. Future investigations should focus on optimising reagent dosage, treatment temperature, and residence time to better control the formation of soluble phosphate phases and maximise lithium recovery. Further work is also required to fully understand the reaction mechanisms responsible for the formation of NASICON-type structures and other lithium- and sodium-phosphate compounds. In addition, the possibility of selectively producing high-value functional materials, rather than simply recovering individual elements, represents an attractive research direction. The integration of phase transformation control, selective leaching, and advanced materials synthesis could ultimately transform LFP black mass from a waste stream into a precursor to produce functional phosphate-based materials for electrochemical applications.

In a broader perspective, the results obtained in this thesis suggest that future phosphorus recovery technologies should move beyond conventional extraction approaches and focus on the deliberate engineering of crystalline phase transformations. Such strategies may offer new opportunities not only for resource recovery but also for the generation of value-added materials from secondary resources.

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