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**VOLCANO-SEDIMENTARY ROCKS FOR GREEN
TRANSITION: VALORIZATION AND RECOVERY FOR THE
DESIGN OF SUSTAINABLE MATERIALS**

ROCCE VULCANO-SEDIMENTARIE PER LA TRANSIZIONE VERDE:
VALORIZZAZIONE E RECUPERO PER LA PROGETTAZIONE DI MATERIALI
SOSTENIBILI

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ABSTRACT

Italy has limited natural resources, but its volcanic regions are rich in volcanic-sedimentary rocks like pumice, lapillus, and zeolitized tuffs, which are commonly used, for example, in floriculture, landscaping, and construction. However, the mining and processing of these raw materials produce scraps with little commercial value, especially pumice and lapillus with grain size smaller than 3 mm. If unsold or not used for quarry rehabilitation, these scraps lead to additional operating costs due transportation and storage in authorized quarry areas, which also requires the payment of regional fees. Currently, over 350,000 m³ of unsold scraps are accumulating, with management costs exceeding €2.50 per cubic meter.

The volcano-sedimentary rocks mentioned above, being natural aluminosilicate raw materials, offer interesting opportunities for valorization in a circular economy perspective. This approach was carried out through a set of study (including bibliographic) and laboratory activities aimed at defining the formulation of mixtures and the characterization of prototype tiles, cement mortars and fertilizers enriched with micronutrients, of which, a brief description follows.

Pumice and volcanic lapillus have been used in different percentages to replace foreign feldspars in the production of porcelain stoneware bodies, with the aim of obtaining naturally colored supports, reducing the use of artificial dyes and maintaining the same technical characteristics of the product. The pieces were produced on a laboratory scale, glazed and fired within the industrial production cycle (48 minutes at 1210°C). The subsequent characterisation allowed the prototypes to be classified as porcelain stoneware belonging to the BIa group (WA 0.5%, B.S.>35 MPa) in accordance with UNI EN 14411 ISO 13006. In addition, a comparative life cycle analysis was carried out between commercially available glazed porcelain stoneware and those containing pumice and volcanic lapillus scraps. The results showed environmental benefits, with a reduction in impact ranging from 8% (freshwater aquatic ecotoxicity category) to 48% (acidification category).

Cementitious mortars have been designed with the aim of reducing the CO₂ emissions associated with the production of the main cement component, clinker, in which the carbonate fraction thermally decomposes at high temperature. Volcanic lapillus was used both as a supplementary cementitious material (SCM) and as a fine aggregate in the production of mortars, with 5, 10, 15 and 20% replacements. The samples obtained were characterized to evaluate their mechanical, physico-chemical and microstructural properties, showing promising results compared to traditional cementitious mortars in the case of substitution as SCM.

Controlled-release Zn fertilizer formulations were also developed and subsequently characterized and tested as foliar fertilizers on *Vitis vinifera*. The formulation composed of 70% zeolitized tuff and 30% pumice scraps showed greater resistance to leaching, under simulated rainfall, than the reference commercial fertilizer. In addition, the potential of pumice waste as Mn^{2+} carriers for foliar fertilization was examined and compared with that of zeolitized tuff. Pumice showed better stability in enrichment and release, making it a promising material for Mn^{2+} delivery to crops.

Keywords: Pumice rock, lapillus rock, porcelain stoneware, cementitious mortar, fertilizers

RIASSUNTO

L'Italia è un Paese relativamente povero di materie prime, ma grazie alla natura vulcanica di alcune sue regioni ospita giacimenti di rocce vulcano-sedimentarie come pomici, lapilli e tufi zeolitizzati, utilizzate nei settori della floricoltura, del verde tecnico e dell'edilizia. Tuttavia, le attività di estrazione e lavorazione di queste materie prime, in particolare per pomice e lapillo, producono sfridi di scarso o nullo valore commerciale. Questi residui, se invenduti o non reimpiegati per il ripristino delle cave, generano costi di gestione legati sia al loro trasporto sia all'accatastamento anche in termini di tasse. Attualmente, la quantità di sfridi invenduti supera i 350.000 m³, con costi di gestione di oltre 2.50 €/m³.

Le rocce vulcano-sedimentarie citate, essendo materie prime naturali alluminosilicatiche, offrono interessanti opportunità di valorizzazione in un'ottica di economia circolare. Questo approccio è stato sviluppato attraverso un insieme di attività di studio (anche bibliografico) e di laboratorio atte a definire la formulazione di miscele e la caratterizzazione di prototipi di piastrelle, malte cementizie e fertilizzanti arricchiti con micronutrienti, dei quali, a seguire, una breve descrizione.

Pomice e lapillo vulcanico sono stati impiegati, in diverse percentuali, come alternative ai feldspati esteri nella produzione di impasti per gres porcellanato, per ottenere supporti naturalmente colorati, riducendo l'uso di coloranti artificiali e mantenendo invariate le proprietà tecniche del prodotto. I manufatti sono stati prodotti su scala di laboratorio, smaltati e cotti all'interno del ciclo di produzione industriale (48 minuti a 1210 °C). La successiva caratterizzazione ha permesso di classificare i prototipi come gres porcellanato, appartenenti al gruppo BIa (WA 0,5%, B.S.>35 MPa), in conformità alla norma UNI EN 14411 ISO 13006. Inoltre, è stata condotta un'analisi comparativa del ciclo di vita tra gres porcellanato smaltato commerciale e quelli contenenti rispettivamente sfridi di pomice e di lapillo. I risultati hanno evidenziato benefici ambientali, con una riduzione degli impatti che varia dall'8% (categoria Ecotossicità acquatica in acqua dolce) fino al 48% (categoria Acidificazione).

Le malte cementizie sono state studiate con l'obiettivo di ridurre le emissioni di CO₂ associate alla produzione del principale componente del cemento, il clinker, in cui all'alta temperatura applicata la frazione carbonatica si decompone termicamente. Il lapillo vulcanico è stato utilizzato sia come materiale cementizio supplementare (SCM) sia come aggregato fine nella produzione delle malte, con sostituzioni del 5, 10, 15 e 20%. I campioni ottenuti sono stati caratterizzati per valutarne le proprietà meccaniche, chimico-fisiche e microstrutturali,

mostrando risultati promettenti se paragonati alle malte cementizie tradizionali nel caso di sostituzione come SCM.

Sono state inoltre sviluppate formulazioni di fertilizzanti a rilascio controllato di Zn, successivamente caratterizzate e testate come fertilizzanti fogliari su *Vitis vinifera*. La formulazione composta dal 70% di tufo zeolitizzato e 30% di sfridi di pomice ha mostrato una maggiore resistenza alla lisciviazione, sotto pioggia simulata, rispetto al fertilizzante commerciale di riferimento. Inoltre, è stato esaminato il potenziale degli scarti di pomice come vettori di Mn^{2+} per la fertilizzazione fogliare, confrontandolo con quello del tufo zeolitizzato. La pomice ha evidenziato una migliore stabilità nell'arricchimento e nel rilascio, risultando un materiale promettente per la distribuzione di Mn^{2+} alle colture.

Parole chiave: Pomice, lapillo, gres porcellanato, malte cementizie, fertilizzanti

GOAL OF THE THESIS

This PhD thesis is part of the New Actions of the PON Programme, funded by ESF REACT-EU, under Action IV.5 "Doctorates on Green Thematics" of the National Operational Programme Research and Innovation 2014-2020. The initiative aims to enhance human capital through doctoral programs focused on strategic issues for environmental sustainability, such as the conservation of ecosystems and biodiversity, reducing the impact of climate change and promoting sustainable development models.

The research project was co-financed by Europomice srl, Milan (Italy), a leading company in the production and marketing of volcanic materials and flux minerals for the ceramic industry. The main aim was the identification and validation of new strategies for the valorization of volcanic scraps derived from the mining operations, which are currently considered by-products or waste due to their poor marketability. Secondly, to support the relaunch of the Italian economy, also the valorization of national natural raw materials such as zeolitized tuffs. In this context, Europomice has joined the project, contributing the supply of volcanic raw materials and the funding of a one-year doctoral scholarship (CUP E85F21003350001) within the doctoral programme in "Industrial and Environmental Engineering" at the University of Modena and Reggio Emilia (UNIMORE). The project, entitled "Volcanic minerals for the green transition (VolMin4GT): Valorization and eco-sustainable recovery of volcanic and melting minerals, and related scrap", is part of strategies for the ecological transition and sustainable use of mineral resources.

An initial focus was placed on volcanic pumice and lapillus with grain sizes less than 3 mm, which currently represent a burden to mining companies due to storage and disposal costs. However, due to their chemical and physical properties, they can be reintroduced into new production cycles in a "circular economy" perspective, transforming a cost into a value.

The approach taken in this research fits into the broader framework of the transition to a more sustainable industry, in line with the Sustainable Development Goals (SDGs) of the United Nations 2030 Agenda. Specifically, the projects developed contribute to the following goals:

- SDG 7 - Clean and affordable energy, promoting the improvement of energy efficiency in industrial processes, with particular reference to the production of building materials, reducing energy consumption and CO₂ emissions;
- SDG 9 - Enterprise, innovation and infrastructure, promoting the use of innovative and sustainable materials to enhance the competitiveness of the industrial sector;

- SDG 12 - Responsible consumption and production, promoting the recovery and reuse of secondary mineral resources to reduce dependence on virgin raw materials;
- SDG 13 - Climate action, contributing to the reduction of greenhouse gas emissions through the partial substitution of energy-intensive materials such as clinker in the cement sector;
- SDG 17 - Partnership for the Goals, fostering collaboration between academia, business and research centers to develop innovative solutions and promote their application on an industrial scale.

The research was developed with an interdisciplinary approach, integrating literature analysis, laboratory experimentation and pre-industrial scale testing, in collaboration with scientific and industrial partners at national and international levels. This synergy between companies and universities was a key element of the project, fostering the creation of strategic partnerships to promote innovation and facilitate the diffusion and adoption of sustainable production models.

The application areas were:

1. Ceramic sector - pumice and lapillus scraps were used to partially replace foreign feldspars for the production of porcelain stoneware body. The goal was to obtain naturally colored supports, reducing the use of artificial pigments and improving the sustainability of the production process. Experimental tests, conducted in collaboration with a company in the Sassuolo Ceramic District (Emilia-Romagna, Italy), CCV Ceramiche Castelvetro, confirmed that the products obtained have properties that comply with international standards (UNI EN 14411, ISO 13006). In addition, the LCA (Life Cycle Assessment) analysis, conducted in collaboration with the Department of Chemical, Environmental and Materials Engineering, of the Higher Polytechnic School of Linares, University of Jaen, Spain (six-month study and research period abroad), showed significant environmental benefits, with a reduction in impacts of up to 48% in the acidification category and 8% in aquatic ecotoxicity compared to conventional formulations.
2. Cement sector - Volcanic lapillus scrap has been tested as a supplementary cementitious material (SCM) and as a fine aggregate in the production of cementitious mortars, with the aim of reducing the use of clinker or the use of virgin sand, the production of which has a high CO₂ emission impact. The substitution, carried out in percentages ranging from 5% to 20%, resulted in mortars with competitive mechanical and microstructural

performance compared to conventional materials for additions up to 15%. The research was carried out in collaboration with Cismondi srl (Piedmont, Italy), a laboratory authorized by the Ministry of Infrastructure and Transport to carry out and certify tests on innovative cementitious building materials.

3. Fertilizer sector – Gradually micronutrients-release fertilizer formulations based on volcanic scraps and zeolitized tuff, enriched with Zn or Mn salts have been developed. Many studies have reported enhanced plant resistance to diseases and pests after supplemental Zn concentrations, or when a mix of micronutrients including Zn was applied. Zn dietary deficiency is related to severe illness as growth retardation and neurobehavioral impairments. Providing Zn to the crops (biofortification) is therefore useful for overcoming soil deficiency, also improving plant immune system response and health. Two options exist, the first involves soil application, however Zn fertilizers (e.g., ZnSO_4) can be easily leached, and the dissolved Zn can interact with soil constituents, forming insoluble and plant inaccessible complexes. Foliar application bypass instead of the soil, however, localized phytotoxicity can occur, as well as leaching from leaves during rain events. Improving Zn permanence and gradual release are therefore two important objectives in foliar application. In this work different formulations were tested, and the most efficient comprised 30 wt% pumice by-product and 70 wt% clinoptilolite-rich zeolitized tuff. This formulation contains about 20 mg/g of exchangeable Zn and exhibits adsorption/release kinetics almost parallel to those achievable using pure raw material. Foliar treatments test carried out in greenhouses on *Vitis vinifera* showed greater resistance to simulated rain leaching than conventional fertilizer ($\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$), promising a possible reduction in treatment dosages and related environmental impact. The research on Mn focused on the use of pumice scraps as carriers for Mn^{2+} to crops for foliar fertilization. Kinetic and Isotherm modelling were performed for Mn^{2+} -enrichment and release, and Mn^{2+} saturation level was compared to the theoretical cation exchange capacity (CEC). Synthetic groundwater was used to simulate agricultural conditions of spraying machines. Pumice scraps were compared with more commonly studied zeolitized tuff (chabazite-rich). Despite its higher amorphous content (87.5 wt%) and lower zeolitic mineral content (analcime; 0.80 wt%), pumice exhibited greater affinity for Mn^{2+} , achieving a higher saturation percentage of the theoretical CEC than the zeolitized tuff. Pumice also demonstrated a more stable enrichment and release, making it a promising material for delivering Mn^{2+} to crops.

The development of these fertilizers was carried out in collaboration with the Department of Chemical and Geological Sciences (DSCG) of the University of Modena and Reggio Emilia.

The results of the three lines of research indicated above demonstrate that volcano-sedimentary rock scraps can be effectively reused in different industries, contributing to the reduction of environmental impact and optimization of natural resources. The recovery of these materials allows not only to reduce industrial sub-products/waste management costs, but also to provide sustainable alternatives to imported or high environmental impact materials.

The integration of the solutions developed into existing production processes, in collaboration with companies and research centers, opens up new perspectives for the dissemination of more sustainable and circular production models, in line with the global challenges of ecological transition and industrial decarbonization.

1. VOLCANO-SEDIMENTARY ROCKS

1.1 STATE OF THE ART

Pumice, lapillus, and zeolite and/or zeolitic tuffs are rocks of volcanic origin that have a number of unique properties, making them particularly suitable for several industrial, agricultural, and environmental applications.

Pumice is a volcanic rock characterized by an extremely porous structure and greatly reduced weight, the result of the rapid cooling of gas-rich acid magma. During this process, gas bubbles become trapped within the solidified material, giving pumice its typical spongy, lightweight texture. This particular genesis gives it a number of distinctive properties: lightweight, high porosity, abrasive capacity and chemical resistance, making it an extremely versatile material in a variety of industrial settings.

Its unique characteristics mean that pumice finds use primarily in the construction industry, where it is used for:

- lightweight aggregate for concrete: *Gündüz and Ugur* evaluated the influence of pumice aggregates of different sizes on the structural properties of concrete, without the use of additives, resulting in a product with strengths comparable to ordinary concrete, but with the advantage of being 30%-40% lighter [1]; *Gündüz* evaluated the effects of pumice aggregate/cement ratios on the properties of low-strength concrete, showing that lightweight nonstructural concrete can be produced by the use of fine, medium, and coarse pumice aggregate mixtures without using admixtures or additives [2]; *Widodo et al.* examined the effects of coarse pumice breccia aggregate content on the casting density and compressive strength of structural lightweight concrete and came to the conclusions that the latter can be produced [3]; *Hariyadi and Tamai* used volcanic pumice as an aggregate replacement material to improve the mechanical properties and quality control properties of porous concrete [4]; *Amel et al.* studied the effect of dune sand and pumice on the mechanical and thermal properties of lightweight concrete obtaining excellent results in terms of compressive strength and Young's modulus [5]; *Rashad and Tanyildızı and Gökalp* have produced interesting and quite comprehensive reviews on the use of pumice as a lightweight aggregate for concrete [6][7];

- supplementary cementitious material: *Hossain* conducted tests on cement where Portland cement was replaced by volcanic ash and pumice powder, obtaining results comparable to those of fly ash cement [8]; *Kabay et al.* studied the effect of partial substitution of Turkish pumice powder and fly ash to Portland cement on physical, mechanical and durability properties, showing that the mixtures with substitutes had comparable long-term mechanical strength to the reference sample, lower water absorption, sorptivity and voids content, and higher resistance to magnesium sulfate than the reference concrete [9]; *Ulusu et al.* evaluated the mechanical, durability and microstructural properties of Portland pozzolanic cement produced with high volume of pumice and showed that pumice is a suitable raw material for the production of sustainable cements [10]; *Aydin* and *Aydin and Baradan* demonstrated that the incorporation of pumice in cementitious mortars improves the high temperature resistance [11][12]; *Rahman et al.* carried out an experimental investigation on the high replacement of cement with pumice in cement mortar and obtained results comparable to those of other authors [13]; *Alqarni* made a useful review of the properties of sustainable concrete using volcanic pumice powder as a supplementary cementitious material [14];
- insulating material: *Binici and Aksogan* and *Celik et al.* conducted investigations on several insulating materials, including pumice, showing that the latter is an attractive material for thermal insulation of buildings [15][16];
- prefabricated building blocks: *Gündüz* investigated the use of mixtures of fly ash, slag, pearlitic pumice and cement to produce cellular hollow lightweight masonry blocks for walls and partitions by demonstrating their possible production [17]; *Sahin et al.* obtained samples of ground pumice aggregates mixed with cement, gypsum and lime, obtaining better physical and mechanical properties than traditional building materials [18].

In addition to the construction sector, pumice is also used in other fields such as: i) filtration: pumice acts as a filter material for the purification of industrial liquids (water, oils and chemicals), as demonstrated by some studies [19][20][21]; ii) catalysts: pumice is used as a porous support for catalysts in various chemical processes [22][23][24]; iii) abrasives: due to its ability to remove impurities and smooth surfaces without damaging them, pumice is widely

used as an abrasive in many industries, including glass and industrial cleaning. In particular, it is used to polish metals, glass, ceramics and composite materials, ensuring a quality finish without affecting the structure of the material being processed; iv) agriculture and horticulture: pumice improves the aeration and drainage capacity of the soil, particularly in hydroponic crops and ornamental plants, in addition to promoting root growth by reducing soil compaction [25][26][27][28]; v) textile industry: pumice is essential in the treatment of denim fabrics to give a "vintage" or worn effect [29].

It is clear from the above that industry is making extensive use of pumice's unique properties, not only as a lightweight and durable building material, but also as an abrasive and a growing medium. Its versatility and sustainability make pumice a material of great interest to industries where efficiency, economy and environmental friendliness are key factors.

Lapillus is a pyroclastic material of volcanic origin, characterized by a porous structure and a composition that includes silicates and various minerals. Its physical properties, including lightness, high porosity and strength, make it a versatile material for numerous industrial applications, mainly in construction, agriculture and environmental purification:

1. Light construction and restoration: Used for hydraulic mortars (plasters and masonry) due to their compatibility with traditional techniques and its burgundy color, which makes it ideal for historical restorations. Suitable for lightweight concretes in roofs, floors and prefabricated buildings due to its low weight and thermal and acoustic insulation capacity. It is difficult to find the term volcanic lapillus in the literature, but it is assumed that it is referred to as red pozzolana/red slag/red tuffs. *D'Ambrosio et al.* collected and analysed mortar samples from the original Roman structures built in central Italy, and their research showed that red tuff with black slag and red and black slag from the local pyroclastic deposit of red pozzolana were used as aggregates for the production of some mortars and concretes [30]. *Rispoli et al.* carried out a detailed archaeometry study of mortar samples taken from columns and walls of the Piscina Mirabilis (Campania, southern Italy), the largest Roman freshwater reservoir ever built. This study highlighted the use of raw materials of pozzolanic origin as the most important components of the Roman recipe for hydraulic mortars [31]. *Altimari et al.* evaluated the possibility of using volcanic lapillus for alkaline-activated materials [32];

2. Drainage and filtration: One of the most recent and promising applications of volcanic lapillus is in the field of environmental remediation. Due to its absorption and adsorption capacity, lapillus is used as a natural filter for wastewater treatment and the removal of heavy metals and other pollutants. Its porous characteristics make it an ideal carrier for bacteria and microorganisms that degrade contaminants, offering an environmentally friendly and sustainable solution for water purification and industrial effluent management. *Bilardi et al.* evaluated the efficiency of a multilayer configuration of a permeable reactive barrier composed of granular mixtures of zerovalent iron and lapillus [33]. *Bilardi et al.* studied the adsorption behaviour of lapillus and pumice through batch tests using nickel- and zinc-contaminated solutions, and it was observed that the adsorption capacity of lapillus is much higher than that of pumice [34]. *Madaffari et al.* made granular mixtures composed of zerovalent iron and lapillus and tested them for nickel removal through column tests, demonstrating their potential in terms of both removal efficiency and long-term hydraulic conductivity [35]. *Bilardi et al.* evaluated the behaviour of granular zerovalent iron/lapillus mixtures and showed that they effectively removed Cu, Ni and Zn from pluralized solutions [36];
3. Rooftop greenery and paving: Due to its water-holding capacity and mineral components, volcanic lapillus is widely used as a soil conditioner and substrate for soilless crops. In agriculture, it improves soil structure, promoting drainage and root aeration, essential factors for healthy plant growth. Lapillus is also commonly used in the construction of roof gardens and green roofs, where it functions as a draining substrate that supports plants and reduces the overall load on the structure, helping to improve the thermal insulation of buildings and manage rainwater. Grain sizes and processing can vary according to specific applications, with materials certified according to technical standards such as UNI EN 13055-1 and UNI 11235 for lightweight aggregates and green roofs. The advantages of using lapillus in the field of green roofs and paving are described by raw material manufacturers[37][38][39];
4. Ceramic and refractory materials: mixed with clays as a demolding agent for ceramic materials and used as a raw material for the production of insulating and refractory materials due to its high resistance to high temperatures.

In brief, volcanic lapillus represents a highly versatile natural resource whose availability and ecological properties make it particularly suitable for applications ranging from sustainable

construction and agriculture to water purification and environmental remediation. Thanks to its singular qualities, lapillus not only meets the needs of numerous industrial sectors, but also contributes to sustainability and energy efficiency, making it a material of growing interest for the future of eco-friendly technologies.

Zeolites are microporous aluminosilicate minerals known for their crystalline structure and ion-exchange capacity, which make them particularly useful in a variety of industrial applications. These materials are widely used in the fields of environmental purification, industrial catalysis, agriculture and energy due to their ability to selectively adsorb molecules and remove contaminants.

Natural zeolites, in economically exploitable quantities, are found in rocks commonly known as “zeolitized tuffs,” also known as “zeolitites.” In this case, the entire rock (without separation of the zeolitic fraction) is used, after any appropriate grinding. There is also a considerable number of synthetic zeolites on the market that can be produced with specific crystallochemical characteristics for the intended use. Over the past 25 years, a total of 182,390 research projects have been carried out. 60,006 of these will take place between 2020 and 2024. The analysis of the existing literature showed some studies based on the following topics:

- Water purification: used for the removal of heavy metals and other pollutants. Their microporous structure and high cation exchange capacity allow the adsorption of toxic metal ions, such as lead, cadmium and copper, making them effective for the remediation of industrial wastewater and the protection of aquatic ecosystems. They are also widely used as filters in drinking water treatment systems, as they remove impurities without adding harmful chemicals to the treated water. *Irma et al.* wrote a review on modification strategies to mitigate nitrogen-containing pollutants from water and wastewater [40]; *Álvaro de Jesús Ruíz-Baltazar* analysed advances in nanoparticle-modified zeolites for sustainable water treatment [41]; *Sossou et al.*, *Abdelwahab and Thabet*, *Iqbal et al.* and *Senthil Rathi et al.* focused on natural zeolites, composites and zeolite nanocomposites [42][43][44][45];
- Catalysts: due to their high surface area and ion exchange properties, zeolites are used in catalytic cracking processes for the production of petrol, diesel and other petroleum products. Specifically, zeolites improve the efficiency and selectivity of the hydrocarbon conversion process, reducing the cost and environmental impact of production. Synthetic zeolites are commonly used for their strength and ability to

withstand high temperatures and pressures, key characteristics in cracking reactions. *Cardoso et al.* used zeolite beta as a catalyst for the catalytic cracking conversion of a bio-oil compound [46]; *Zhang et al.* studied a zeolite capsule catalyst for the direct synthesis of liquefied petroleum gas from syngas [47]; *Zandonai et al.* worked on extending the lifetime of the catalyst used for the production of synthetic oil-like fuel [48]; *Shimada et al.* developed a titanium-modified zeolite-based catalyst for the hydrocracking of heavy oil [49];

- Agriculture: zeolites are used as soil improvers and growing media. Due to their ability to retain nutrients and release them slowly into the soil, zeolites help improve fertilizer efficiency and reduce nutrient losses through leaching, a phenomenon that can deplete soil and damage groundwater. *Javaid et al.* discussed the role of zeolites in improving soil physicochemical characteristics and plant performance [50]; *Galardini et al.* enriched zeolites with nitrogen to improve soil microbial physiology and mitigate fertilizer-derived CO₂ emissions from arable land [51]; *Yadav et al.* demonstrated that zeolite is a viable substrate for adsorbing and desorbing nutrients in swine manure to fertilizer [52]; *Songara et al.* prepared and characterized a nanocomposite hydrogel with zeolite showing that it can be used as a soil conditioner and nutrient carrier [53]; *Flores et al.* synthesized zeolites from coal fly ash using it as a potash fertilizer for wheat cultivation [54]; *Bernardi et al.* described the characterization and application of Brazilian zeolitic sedimentary rocks as a slow plant fertilizer and soil conditioner [55]; *Reháková et al.* discussed agricultural and agrochemical uses of natural zeolite of the Slovak clinoptilolite type [56];
- Construction: zeolite can be used as an additional cementitious material in concrete as it improves its strength, durability and workability. Due to its ability to reduce heat of hydration, it is particularly useful in solid concrete structures, where it helps prevent cracking. In addition, zeolite is used in the production of lightweight building materials, offering excellent thermal insulation properties and reducing the weight of structures. Zeolite products further improve the energy efficiency of buildings due to their insulating capabilities. Zeolite's natural ability to absorb and release moisture makes it ideal for materials designed to regulate indoor microclimate, providing a more comfortable living environment [57][58][59][60][61][62][63][64].

Zeolites provide innovative and sustainable solutions in a range of industrial sectors. From water purification to petrochemical catalysis, from agriculture to greenhouse gas emission

reduction, zeolites represent a material of high versatility and relevance to the future of sustainable technologies.

1.2 PUMICE ROCKS, VOLCANIC LAPILLUS AND ZEOLITIC TUFF

The materials, focus of the present work, were pumice rock, volcanic lapillus and zeolitic tuff. These geomaterials were supplied by Europomice S.r.l., a mining company which, through the conscious exploitation of its mineral resources, over the years has achieved a leading position in the production and marketing of volcanic aggregates that meet the needs of the floriculture, technical green and construction sectors. The Company began its mining and processing of volcanic aggregates in the late 1980s, taking over and upgrading some existing production units located on the border between Tuscany and Lazio, in the region surrounding Lake Bolsena (Italy). To these production units is to be added the mining concession located in the province of Sassari (Sardinia, Italy), between the municipalities of Anela and Bono, lying between the southeastern slopes of the “Goceano chain” and the extensive granite outcrops of the Serra di Orotelli.

Pumice is mined in Tuscany, in Pitigliano (GR) at “Poggio Nardecì” (**Figure 1.1**), and in Lazio, in Tessennano (VT) at “Riserva Muraccio” and Arlena di Castro (VT). Volcanic lapillus and zeolitic tuff (chabasite containing) are mined in Lazio, in Cellere (VT) at “Monte Cellere” (**Figure 1.2**) and in Tessennano (VT) at “Riserva Muraccio” (**Figure 1.3 left**) respectively. Zeolitic tuff, clinoptilolite containing, is mined in Sardinia in the municipality of Bono (**Figure 1.3 right**).

Pumice rock and volcanic lapillus were chosen because of the mining and production of commercial granulometry yields material that turns out to have little market because it is very small in size, less than 3 mm in diameter; for the company this material represents a by-product, since it is not actually the product on which processing is directed. By-products are production waste that can be managed as goods and not as waste if they meet the requirements of the law [65]. Such extraction scrap, therefore, is not a waste, but its management becomes problematic since, if unsold, there can be two alternatives:

(a) it is used as restoration from the same quarry, in which case it is subject to an additional transportation cost from the plant to the quarry;

(b) it is piled in areas within the quarry's jurisdiction (authorized as an internal landfill at the quarry) and then resold from these areas but paying a regional fee.

Both solutions, therefore, imply costs that to date are quantified at more than 2.5 €/m³, therefore, it becomes strategic to try to valorize these national volcanic aggregate scraps.

Zeolitic tuff was not selected as a by-product or waste, since there are no grains of little commercial interest from the extraction and processing of the rock, but for its unique properties, which are particularly useful in agriculture. Indeed, in organic farming, micronized zeolitic mineral powder is an effective natural treatment for foliar protection against pests, as well as enhancing plant resistance to biotic and abiotic stresses. Due to their high cation exchange capacity, zeolitic structures can also facilitate the production of slow-release fertilizers. However, their large-scale use is limited due to high costs. Therefore, zeolitic tuffs were used as a reference support in order to evaluate supports obtained by recreating mixes based on zeolitic tuffs and pumice rock or lapillus.



Figure 1.1. Pumice quarry located at “Poggio Nardecì” (Pitigliano (GR), Italy).



Figure 1.2. Lapillus quarry located at "Monte Cellere" (Cellere (VT), Italy).



Figure 1.3. Chabasite-type zeolitic tuff quarry on the left (Tessennano (VT), Italy), clinoptilolite-type zeolitic tuff quarry on the right (Bono (SS), Italy).

1.3 GEOLOGICAL OVERVIEW

1.3.1 QUARRIES IN CENTRAL ITALY

The quarry units found in central Italy and mentioned in section 1.1 (regarding the extraction of pumice rock, volcanic lapillus, and chabasite-based zeolitic tuff) are located, from a strictly geological point of view, in the area between the Vulsino volcanic district, which extends from southern Tuscany to the northernmost part of Lazio, in the area of Lake Bolsena, and the Cimino-Vicano volcanic district, which is located further south than the previous one, in the area of Lake Vico (**Figure 1.4**).

The geologic-deformational history of the Lazio volcanic area must be framed within the tectonic-dynamic evolution of central Italy. The geological evolution of volcanic apparatuses is the result of geodynamic processes and of the distensional tectonics of the belt between the Apennine chain and the Tyrrhenian coast, following the Apennine orogeny and active from the Late Pliocene until about 50,000 years ago. Geodynamically, Lazio volcanism is related to the extensional tectonics responsible for the formation of the Tyrrhenian basin in the post-Miocene. In fact, since the Pliocene, an intense magmatic activity began that, along the Apennine line, involved a vast area from Mount Amiata to Campania.

The volcanoes of Lazio belong to two clearly distinct magmatic series: the first includes the acidic, rhyolitic and rhyodacitic volcanism of the Cimino, Tolfa and Ceriti mountains and is older (between about 2 and 1 Ma) than the second series, which includes the Vulsino, Vicano, Sabatino and Colli Albani groups, and which has a distinct alkaline-potassic character and was active between 0.8 Ma and the present. Latium thus represents the junction of these different systems.

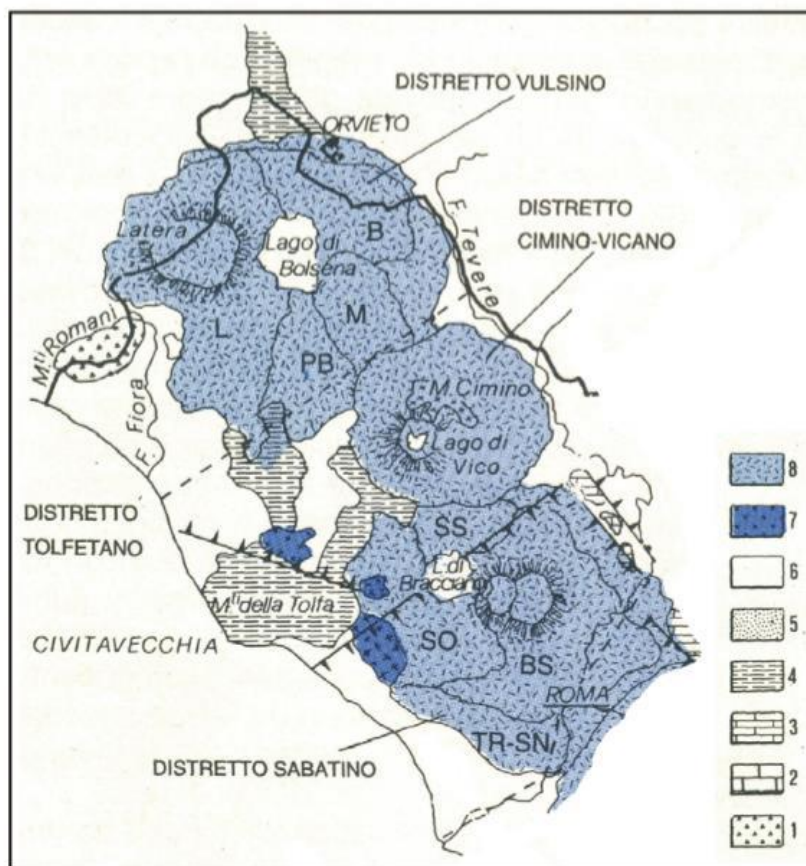


Figure 1.4. Main volcanic complexes of northern Latium. Legend: 1: metamorphosed basement rocks; 2: sediments of the Latium-Abruzzo platform; 3: sediments of the Umbria-Marchigiano basin; 4: allochthonous sediments of the Ligurian and

Subligurian complex; 5: allochthonous flyschoid sediments; 6: sandy-clayey-gravel neoautochthonous sediments; 7: volcanic districts with acid to intermediate chemism; 8: volcanic districts with potassic to highly potassic character (PB: Paleobolsena volcanic complex; B: Bolsena volcanic complex; M: Montefiascone volcanic complex; L: Latera volcanic complex; SO: western sector activity; SS: northern sector activity; BS: Sacrofano-Baccano complex; TR-SN: Red Tuff black-slag pyroclastic flow) [66].

The Vulsino Volcanic District, which is the northernmost of the volcanic districts in Latium and occupies an area of about 2200 km² between the Fiora River and the Tevere River, and which sees the prevalence of subaerial activity, mainly of an explosive nature, is undoubtedly the most complex of the Tuscan-Latium volcanic apparatuses. It is situated at the intersection of a complex system of faults with Apennine and anti-Apennine direction. This apparatus has been the protagonist of the most impressive and extensive volcanic manifestations in the region: during its activity, there has been the emission of a great variety of volcanic products (ignimbrites, lavas, pyroclastites of various kinds) attesting to an activity that, which began in the Pleistocene, has lasted until very recent times and is still ongoing in hydrothermal and sulfataric form [67]. The sedimentary substrate consists of neo-autochthonous post-orogenic deposits of the Upper Miocene and Pleistocene, covering flysch units and Mesozoic carbonate successions of the Tuscan and Umbro-Marchigiano domains [68]. The emission centers, almost always arranged along fractured lines, can be mostly located around the two depressions of Latera and Lake Bolsena (**Figure 1.5**). The former must be considered as the terminal caldera of a complex stratovolcano; the latter must be interpreted as a large collapse basin identified in several successive phases and whose subsidence was controlled by regional fault systems. These fractures formed the pathway for rising magmas that gave rise to a series of eruptions with predominantly lava and ignimbritic products, characteristic of the Bolsena and Bagnoregio areas. The final activity along these fractures was extruded through modest point eruptions, evidenced by a series of aligned cones, with emissions of tuffs, slags, and modest lava flows.



Figure 1.5. Location of the Latera and Lake Bolsena depressions [69].

The Cimino Volcanic District was active in the Pleistocene and particularly between 1.35 and 0.95 Ma, an interval in which the upwelling of acid viscous magmas from regional fractures resulted in the formation of more than 50 domes and stagnation domes, as well as the emplacement of pyroclastic deposits from surge and concentrated flows. Volcanic products are mainly latites and trachytes.

The activity of the Vicano Volcanic District, between 0.8 Ma and 0.09 Ma, developed mainly from a central edifice, the Vico volcano. It is a typical strato-volcano with the end truncated by an eccentric caldera to the south, sunk to form the lake of the same name. From the bottom of the caldera rises a secondary edifice, the volcano of Monte Venere. However, the present morphology is not determined by the mere existence of an original crater, but by the calderic sinking of the central part of the ancient edifice. The products of the Vicano Volcanic District cover much of those of Cimino and are evidence of explosive and effusive phases. In fact, several Plinian fall deposits, lavas and several pyroclastic flows of leucitic, tephritic-phonolitic and phonolitic-leucitic nature are present [67].

1.3.2 ZEOLITIC TUFF MINE OF SARDINIA

The area affected by the mining referred to in Section 1.2 with respect to the clinoptilolite type zeolitic tuff is part of a context characterized by the contact between Paleozoic metamorphic rocks (to the north) and granitoid intrusions (to the south). To the south, there are granitic outcrops with a specularly variable tonalitic-granodioritic composition, in an area affected by faults that lowered the surfaces where the formation of interest was deposited, represented by volcanites that recolored a preexisting morphological and/or tectonic depression, preserving it from erosion, which is still active in the surrounding slopes. To the N-NW, Paleozoic shales of low to medium metamorphic grade, sometimes affected by contact metamorphism with the granitic batholith that forms the basement of Goceano, are exposed. The mine is located on the eastern margin of a broad structural depression known in the literature as the "Sardinian Trench", which is composed of a series of E-NE trending Oligo-Aquitania transcurrent basins, overlain by other basins of general N-NW extension.

The main structure of the sector is represented by the granitoid lithologies of the basement. These are light-colored, holocrystalline magmatic rocks with isotropic and hypidiomorphic granular textures of variable chemism, generally classified as tonalite-granodioritic and diorite-tonalitic grains originated from magmatic cores of early differentiation, sometimes located at the edges of syn-tectonic plutons. Oligo-Miocene volcanic rocks belong to the so-called "Calalkaline Volcanic Cycle" dating back to the Tertiary Era [70]. They are related to the early stages of the Alpine Orogeny (ca. 30 MA) with the related rift system that affected the entire western Mediterranean during the same period and to the formation of the "Sardinian Oligo-Miocene Trench" (ca. 30 MA), which crosses the island in a meridian direction from the Gulf of Cagliari to the Gulf of Asinara. These lithologies can be attributed to the lower ignimbritic series.

Today, the different facies that can be observed are related to the different positional characteristics and subsequent reworking of sub-aerial or fluvio-lacustrine environments, which locally resulted in apparently very different rocks, but with similar rhyolitic-riodacitic chemism.

In the concession area, these ignimbrites occur in moderately cemented tuffaceous or tuffitic or lithoid layers, sometimes altered by probable hydrothermalism, with thickness ranging from a few meters to tens of meters. Such hydrothermalism of the vast surrounding area suggests zeolitization due to transport of hydrothermal fluids from basement fractures.

1.4 MATERIALS AND METHODS

1.4.1 CHEMICAL AND PHYSICAL CHARACTERIZATION

Approximately 1,000 grams of a well-mixed sample was taken from each mineral, in order to have a representative sample of the entire bank of material (quartering method). The samples were subjected to particle size analysis, chemical and mineralogical analysis, pH and specific conductivity measurements, true density, and finally investigated with the scanning electron microscope (SEM). Before performing the analyses, the samples were dried in an oven for 24 hours at a temperature of $100\pm 5^{\circ}\text{C}$.

The *particle size analysis* was performed by taking 100 grams of sample and sieving it first manually, using stacked certificated sieves with an average hole diameter of 2 mm and 1 mm, to separate the coarse fraction from the fine one, and then with a laser particle size analyzer (Malvern Instruments, model Hydro200S).

Chemical analysis was performed by sequential X-Ray Fluorescence Spectrometer (XRF) model ARL PERFORM'X while mineralogical analysis was performed by X-ray diffraction system, model X'PERT 3 POWDER PANALYTICAL with Rietveld method. The phase fractions were extracted by the Rietveld refinements, using GSAS software and they were rescaled on the basis of the absolute mass of corundum originally added to the mixtures as an internal standard. Chemical and mineralogical analysis was provided by the volcanic raw material company.

In order to evaluate the chemical stability of the samples by assessing the release of ions into the aqueous environment, *pH* and *specific conductivity* measurements were carried out using a portable pH tester (Laboratory PH sensor Hamilton type Liq-glass SL, OAKTON Eutech Instruments pH 5/6 and Ion 6) and a portable conductivity tester (OAKTON Eutech Instruments CON6/TDS 6), respectively. Few grams of sample were taken and placed inside a beaker containing bi-distilled water with a sample-water ratio of 1:10. The test was performed in dynamic mode (700 rpms) for 8 hours; measurements were taken at specific times, i.e., at the initial instant and after 5, 15, 30, 60, 120, 240 and 480 minutes. The above reported procedure is in line with UNI EN 13037:2012 (pH rule standard) and UNI EN 13038:2012 (conductivity rule standard).

True density (ρ_{abs}) measurements were assessed for each mineral with a helium pycnometer (Mycrometrics Accupyc 1340) by taking a few grams of sample and placing them inside a 10

cm³ measuring cell. Bulk density (ρ_{bulk}) was measured by Geopyc 1360 Envelope Density Analyzer (Micromeritics). In this analysis, the sample is placed in a cylindrical chamber equipped with a piston. The measure is run before with the empty chamber to determine the total volume and after with the granular sample. The volume of the sample is determined by subtracting the volume of the empty chamber from the volume of the same chamber after the sample has been added.

Microstructural analysis was conducted using the scanning electron microscope (SEM), model ESEM-Quanta 200, coupled with an X-ray EDS microanalysis system model X-EDS Oxford INCA-350.

1.4.2 THERMAL CHARACTERIZATION

Thermal analyses were performed on the materials in order to be able to understand the possible fields of their use. The thermal transformations of the materials were analyzed by means of thermo-gravimetric analysis and differential thermal analysis (TGA/DTA) and using hot stage microscopy (HSM). Samples were appropriately ground with an agate mortar to avoid possible contamination and powdered, reaching an average particle diameter of less than 20 μm . The samples were analysed with a heating rate of 10°C/min.

DTA allows to determine the thermal reactivity of the powders as the temperature increases, while *TGA* allows to establish the change in mass as a function of temperature resulting from the development or absorption of gases. The TGA/DTA analysis was performed simultaneously with the NETZSCH STA 429 (CD) instrumentation.

The *analysis HSM* was performed with Expert System Solutions instrumentation, mod. M3MD1600/80/2. The samples were first reduced to powder and then pressed to form very small cylinders 2 mm in diameter and 3 mm in height. Images were taken at a heating rate ramp (10°C/min) until 1300°C. During the post-analysis phase, by means of calculations on the shape of the specimen, the instrument software is able to attribute the characteristic temperatures of the transformation states (sintering, softening, sphere, hemisphere and melting temperatures) for each sample analyzed.

1.5 RESULTS AND DISCUSSION

1.5.1 PARTICLE SIZE DISTRIBUTION

The particle size distribution was carried out only on pumice rock and volcanic lapillus because they are mining scraps, and it is interesting to evaluate the fraction less than 3 mm because they are natural raw materials that have very poor marketing and therefore are considered by-products; while for zeolitic tuffs all particle sizes are suitable for industrial and agronomic purposes.

The size distribution is very important because in some sectors, such as ceramics, a finer particle size is required to increase powder reactivity and reduce milling and mixing times; while in other sectors, such as agronomy, all sizes are suitable because they have applications specific.

The following graphs are for the particle size distribution of the sample with an average diameter of less than 1 mm (as described in *section 1.4.1*). Two curves are shown on a semilogarithmic scale: a cumulative curve (the corresponding y-axis is on the right) and a bimodal distribution curve; characteristic diameters are also shown (d10, d50 and d90).

Figure 1.6 shows the particle size distribution of pumice rock. Out of 100 g of sample, 27% has $\varnothing > 2$ mm, 31% has $1 \text{ mm} < \varnothing < 2$ mm, and the remaining 42% has size less than 1 mm in diameter. The fraction with $\varnothing < 1$ mm was analyzed by Laser Granulometer: 90% of the distribution is $< 278 \mu\text{m}$ and 100% $< 851 \mu\text{m}$. D50 indicates that the 50% of the distribution is under $22\mu\text{m}$.

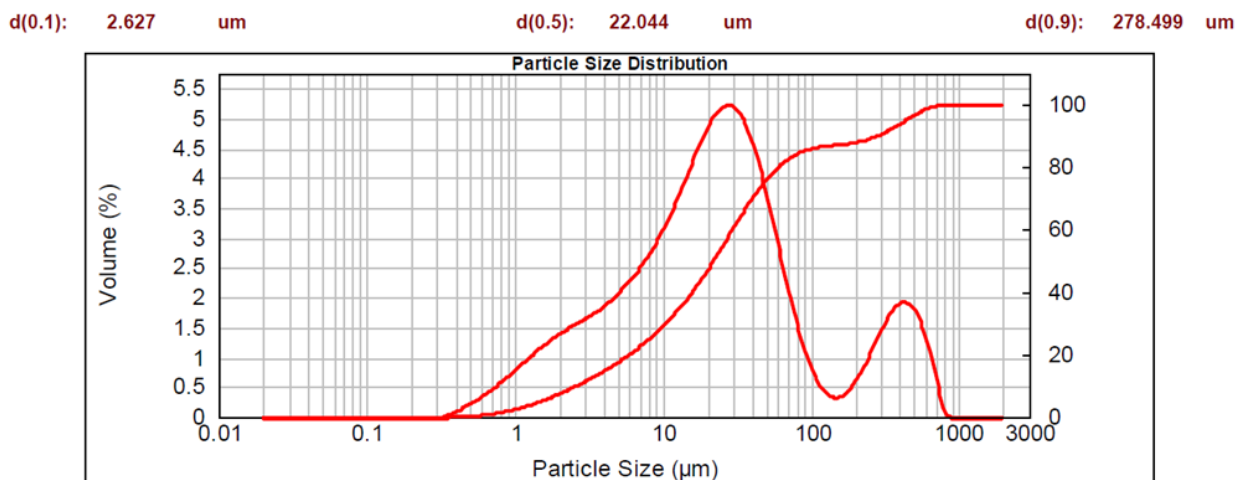


Figure 1.6. Grain size distribution of pumice rocks.

Lapillus presented the following particle size distribution: 6.5% had diameters greater than 2 mm, 17% had diameters between 1 mm and 2 mm, and the remaining 76.5% had diameters of less than 1 mm. From the reported data in **Figure 1.7**, 90% of the distribution is under 65 μm and 100% under 753 μm . D50 means that 50% of the distribution is under 22 μm .

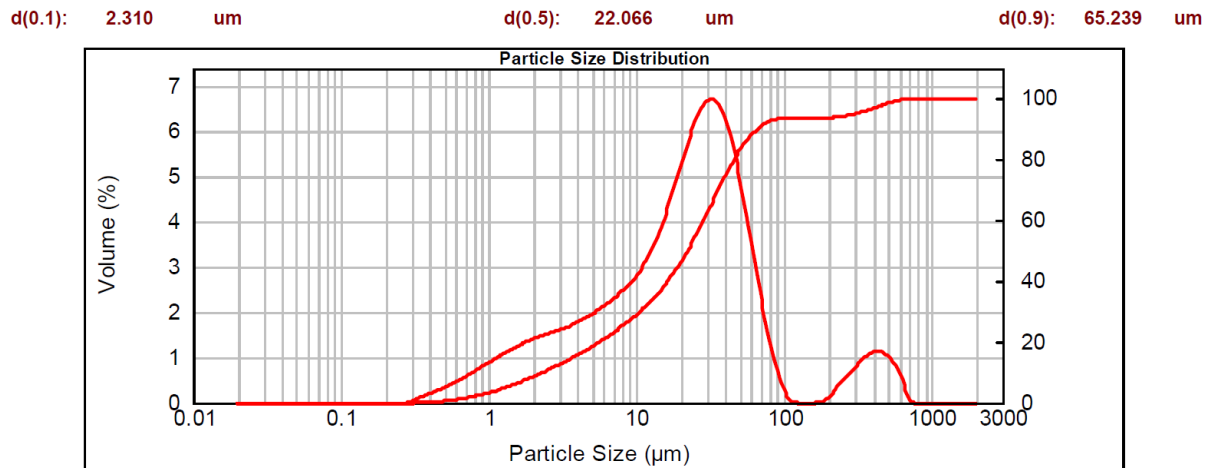


Figure 1.7. Grain size distribution of lapillus.

Looking at the d90 of pumice rock and lapillus, it is possible to say that the particle size distribution of lapillus is finer than that of pumice: 90% of lapillus has an average diameter < 65 μm while only 81% of pumice particles have an average diameter below this value.

1.5.2 CHEMICAL AND MINERALOGICAL ANALYSIS

Chemical analyses of the main elements (Si, Al, Fe, Mg, Ca, Na, K, Ti) for pumice, lapillus and two kinds of zeolites, carried out by X-ray fluorescence of the raw materials, are shown in **Figure 1.8**.

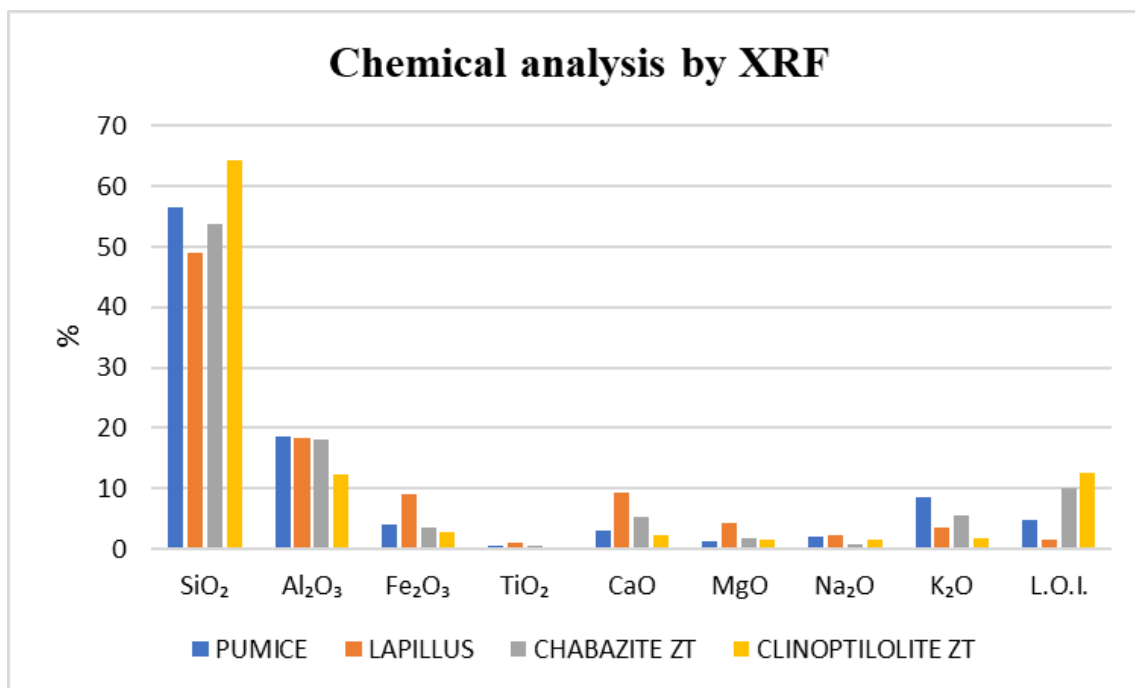


Figure 1.8. XRF analysis of raw materials.

The highest SiO₂ content is associated with clinoptilolite based zeolitic tuff (over 60%).

Fe₂O₃, CaO, MgO, K₂O and Na₂O were detected in all materials. Lapillus had a higher Fe₂O₃ and CaO content than the others. The content of K₂O is higher in pumice and in chabazite-based zeolitic tuff. In chabazite-based zeolitic tuff, the content of Na₂O was lower if compared with the other materials. The ignition loss of zeolitic tuffs is higher than others, but this is due precisely to their nature since zeolites are hydrated alumino silicates.

Mineralogical analyses are visible in **Table 1.1**.

Table 1.1. Mineralogical analysis of raw materials.

MINERALOGICAL ANALYSIS				
	Pumice	Lapillus	Chabazite ZT	Clinoptilolite ZT
Quartz (SiO₂)	1.1	-	-	5.2
Sanidine (K,Na)(Si,Al)₄O₈	11.2	19.8	21.4	-
Anorthite (CaAl₂Si₂O₈)	3.0	26.4	-	-
Amorphous fraction	79.7	16.1	-	11.9
Chabasite (Ca,Na₂,K₂,Mg)Al₂Si₄O₁₂•6H₂O	-	-	46.8	-
Clinoptilolite (Ca, K, Na)₃₋₆(Si₃₀Al₆)O₇₂ • 20(H₂O)	-	-	-	66.2
Heulandite (H₄CaAl₂ (SiO₃)₆•3H₂O)	-	-	-	1.1
Analcime (Na[AlSi₂O₆] • H₂O)	0.6	6.1	-	-
Diopside (CaMgSi₂O₆)	-	19.0	-	-
Muscovite (K₂Al₄(Si₆Al₂O₂₀)(OH)₄)	3.8	-	-	-
Phlogopite KMg₃(Si₃Al)O₁₀(F,OH)₂	0.6	-	2.5	-
Hematite (Fe₂O₃)	-	4.9	-	-
Plagioclase (NaAlSi₃O₈--CaAl₂Si₂O)	-	5.8	-	10.6
K-Feldspar (KAlSi₃O₈)	-	-	-	-
Mica/Illite (K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂,(H₂O)]	-	1.9	-	5.0
Other	-	-	29.3	-

Mineralogical analysis showed that all the products under investigation, except of chabazite-based zeolitic tuff, exhibited an amorphous fraction; this was low in clinoptilolite-based zeolitic tuff and lapillus and very high in pumice. Sanidine is present in pumice, lapillus, and chabasite-type zeolitic tuff. Anorthite has been detected in both pumice and lapillus. Muscovite is present only in pumice while hematite and diopside only in lapillus. Plagioclase and mica/illite are present in both lapillus and clinoptilolite-type zeolitic tuff. One interesting thing is the presence of analcime, a zeolitic species, in lapillus and pumice.

The potassium content in pumice, which is higher than in other materials, may derive from sanidine and muscovite. The high iron and calcium content in lapillus may be associated with the presence of hematite, anorthite and diopside. The two zeolitic tuffs have a higher loss on ignition, this could be due to the presence of interlayer water.

1.5.3 pH, SPECIFIC CONDUCTIVITY AND DENSITY

pH and specific conductivity were measured under stirring conditions and their trends are reported in **Figure 1.9** and **Figure 1.10**. From the plots it appears evident that pH values are all very similar and near to neutrality. Clinoptilolite shows lower values which can be correlated to the lower amount of alkaline elements in the chemical analysis. On the other hands, conductivity shows more significant differences among the different volcanic materials and an increasing trend with time. The behaviour is in line with the chemical analysis, with higher values for rocks containing a higher amount of alkaline elements. Specific conductivity was not conducted on clinoptilolite-based zeolitic tuff. The tests were conducted on granular material while the clinoptilolite-based tuff was μm -sized, so the comparison of values would not be representative.

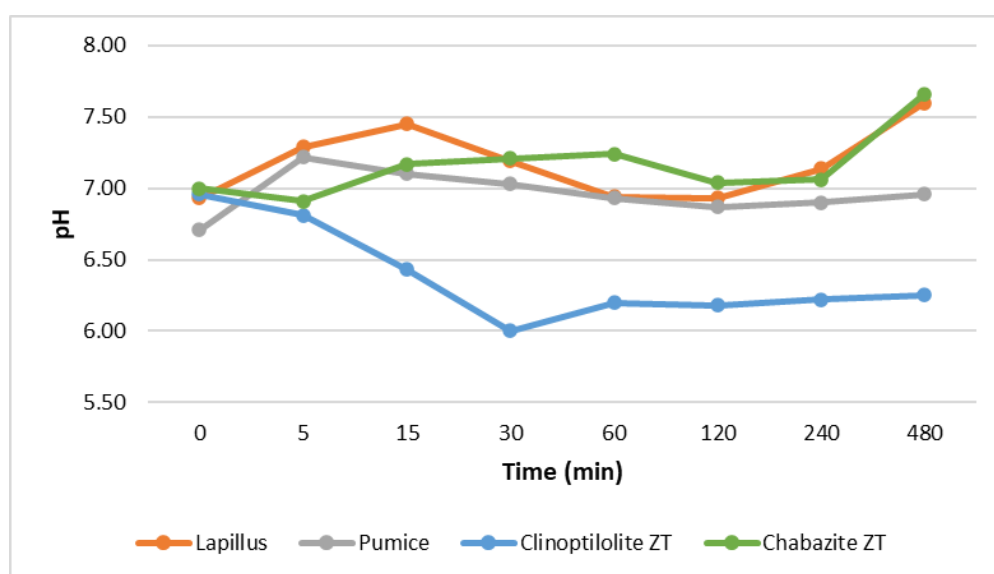


Figure 1.9. pH: stirring condition.

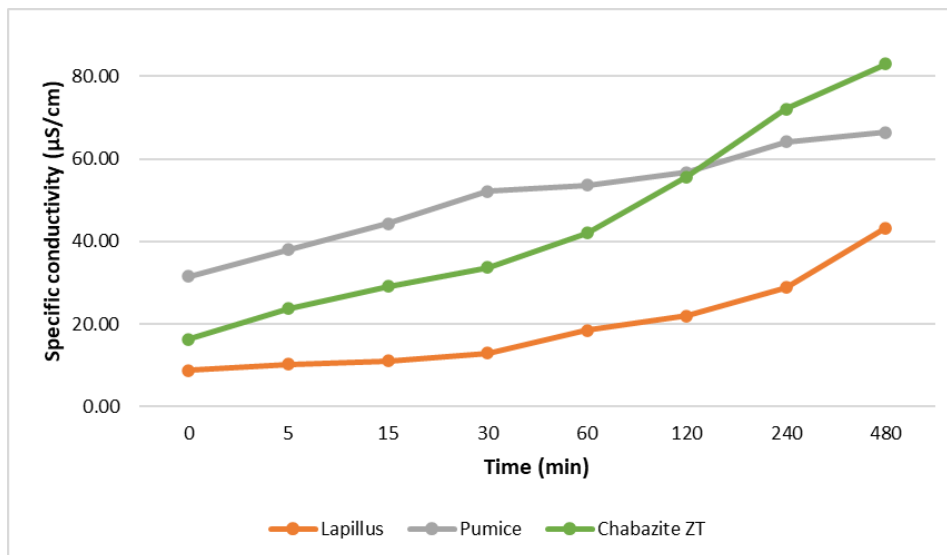


Figure 1.10. Specific conductivity: stirring condition.

The true and bulk density values for each material can be seen in **Table 1.2**.

Table 1.2. True and bulk density data for all the rocks analyzed.

Samples	True density (Kg/m ³)	Bulk density (Kg/m ³)
Lapillus	2843.8±0.6	750-1150
Pumice	2579.3±1.6	480-880
Chabazite ZT	2284.3±1.1	700-1000
Clinoptilolite ZT	2289.6±0.9	800-1000

True density corresponds to the mass of a particle divided by its volume, excluding open and closed pores. Generally, this kind of density depends on the chemical compositions of volcanic products. Zeolitic tuffs showed a lower true density value than the other products. Lapillus showed a higher density value than the other volcanic rocks while pumice showed an intermediate value. The reported values allowed some considerations to be made: the higher values for lapillus can be related to the presence of higher density crystalline phases such as anorthite (2500-2800 Kg/m³) and hematite (5120-5300 Kg/m³); the values for pumice rock can be related to the presence of crystalline phases such as sanidine (2550-2630 Kg/m³); the lower values of zeolitic tuffs are attributable to the presence of chabazite or clinoptilolite (for both 2200-2400 kg/m³).

Bulk density of a powder is the ratio of the mass of an untapped powder sample and its volume including the contribution of the inter particulate void volume. Hence, the bulk density depends on both the density of powder particles and the spatial arrangement of particles in the powder bed and permits to evaluate the compaction degree of the powder and can be correlated to the porosity.

1.5.4 SEM ANALYSIS

SEM analysis was performed only on pumice rock and lapillus to investigate the microstructure of the materials and understand the possible fields of use. SEM analysis agrees with the mineralogical one confirming that lapillus is more crystalline while pumice is more amorphous.

The microstructural analysis of pumice sample (**Figure 1.11**) showed:

- High amount of particle with size in the range 100-200 μm ;
- Greater interparticle thickening;
- Particles with semi-regular shape and comparable size to each other;
- The presence of non-porous glassy zones (circled in **Figure 1.11b**) corresponding to the vitreous fraction detected by XRD (79.7%).

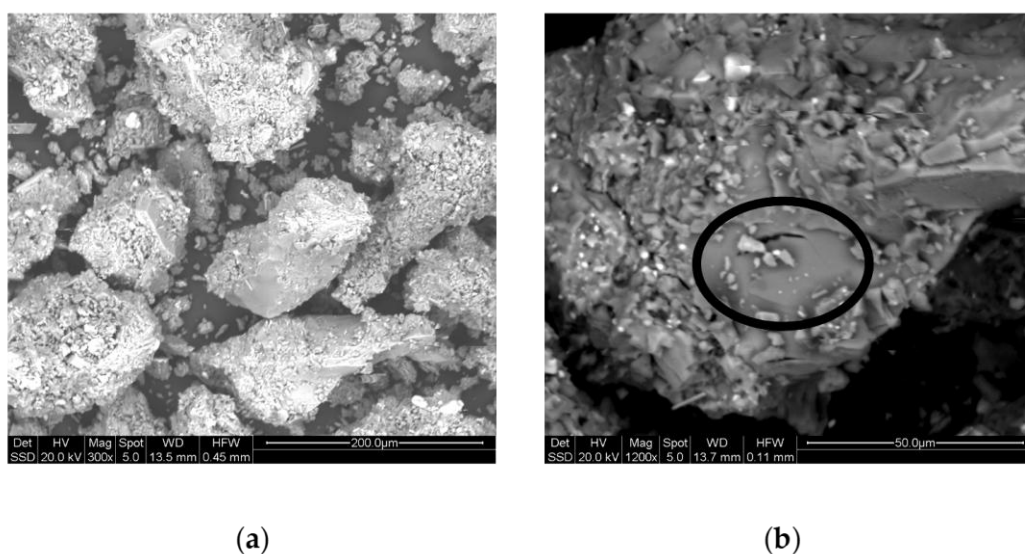


Figure 1.11. Pumice: micrographs at 300x (a) and 1200x (b) in BSE mode.

The microstructural analysis of lapillus sample (**Figure 1.12**) showed:

- Wide grain size range, between 20-400 μm ;
- Low mutual densification between particles;
- Particles with irregular shapes and jagged edges;
- High interparticle porosity regardless of particle size.

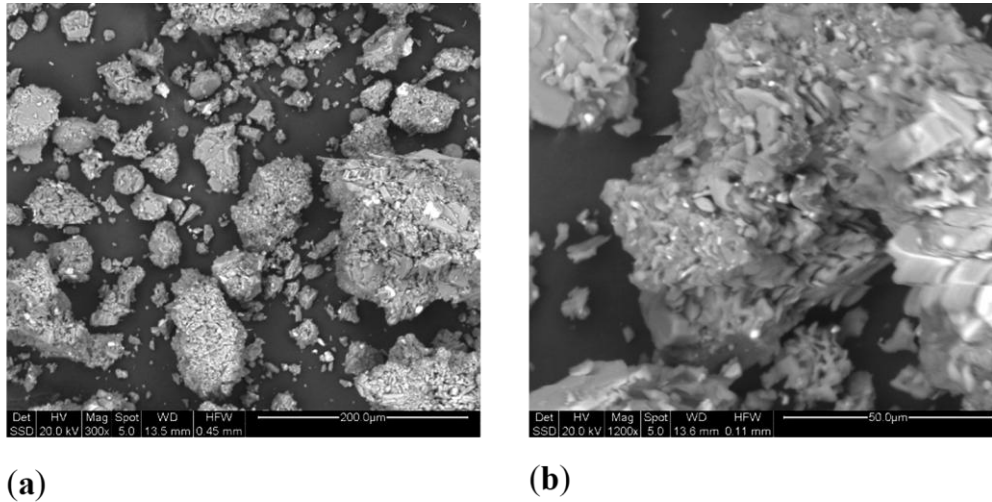


Figure 1.12. Lapillus: micrographs at 300 $\times$ (a) and 1200 $\times$ (b) in backscattered electron (BSE) mode.

With the chemical analysis, described above, the total elements were known, while with the SEM together with the EDS probe it was possible to analyze very small crystalline zones and the amorphous areas to assess the chemical composition of the glassy fraction and the possibility of alkaline activation of the materials.

In **Table 1.3** it is reported the semi-quantitative chemical analysis performed with EDS on pumice rock and lapillus.

Table 1.3. EDS analysis of crystalline and/or amorphous areas in pumice and lapillus samples.

Average chemical composition (EDS)	Lapillus (crystalline zone)	Pumice (crystalline zone)	Pumice (amorphous zone)
O	53.9%	52.6%	61.7%
Si	19.8%	21.5%	16.4%
Al	8.9%	9.4%	6.5%
Fe	5.8%	3.9%	2.7%
K	2.6%	3.7%	0.3%
Na	2.6%	2.8%	Traces
Mg	1.3%	1.6%	4.8%
Ti	0.5%	0.5%	0.4%
Ca	-	4.5%	7.2%
P	0.3%	-	-

EDS analysis confirms the mineralogical characterization showing that the crystalline part of pumice is enriched in Si, Al and K corresponding to the sanidine crystalline phase, while in the amorphous fraction, alkaline earth elements (Ca and Mg) are concentrated together with Si and Al.

1.5.5 THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS (TGA/DTA)

The thermal investigation was conducted only on pumice and lapillus.

The following figures describe the thermograms with their peaks, endothermic or exothermic, and the weight variation of the material under study. The red curve describes the TG while the blue curve describes the DTA.

The behavior of pumice rock when the temperature increase can be seen in **Figure 1.13**.

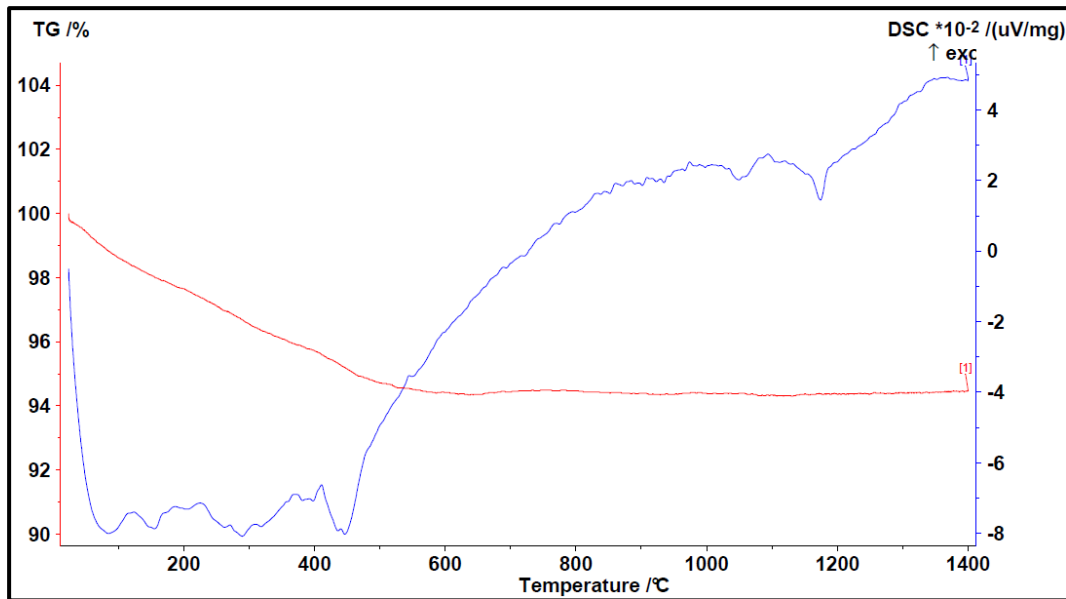


Figure 1.13. Simultaneous TG/DTA analysis of pumice rock.

Pumice rock shows a LOI (Loss On Ignition) of about 6%, visible with TG , with the greatest weight loss at temperatures below 500°C due to moisture removal and that of OH species bound to metal oxides.

With reference to DTA, an endothermic event occurred around 450 °C, which could be due to the dihydroxylation of the muscovite clay. The material remained stable up to around 1000°C and then underwent melting of different crystalline phases at temperatures of around 1050°C and 1200°C showing two separate peaks.

Figure 1.14 shows the results of the analysis conducted on lapillus.

The red curve showed a material with a low LOI, around 1%, indicating its high thermal stability; the sample has a low interstitial water content.

Three main events can be described from the blue curve:

- Up to a temperature of about 200 °C, there was a loss of moisture resulting in a loss of about 0.5% of the initial weight;
- Between 500 °C and 1000 °C, substantial stability of the material was noted during heating;
- Around 1200 °C there was an endothermic peak due to the melting of the crystalline lattice constituting the material, which, as confirmed by the mineralogical analysis data, has an exclusively crystalline microstructure (approx. 87%).

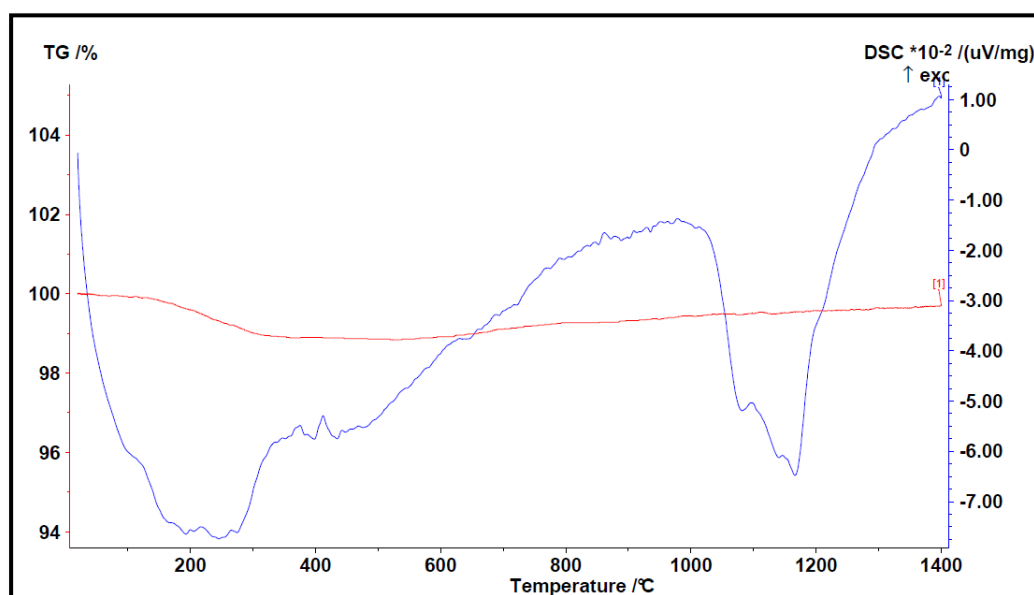


Figure 1.14. Simultaneous TG/DTA analysis of lapillus.

1.5.6 HOT STAGE MICROSCOPY

Hot stage microscopy (**Table 1.4. Characteristic temperatures. Table 1.4**) allowed the characteristic temperatures of the samples to be determined, and their knowledge is helpful in determining optimum ranges of manufacture conditions for ceramic processes. The values given for sodium feldspar were kindly provided by Colorobbia (Italy) for comparison purposes. The feldspar used is very pure and has few impurities (Iron content < 0.05%), so it melts at higher temperatures than less pure feldspars. The melting temperatures of feldspar can vary significantly, typically ranging from approximately 1110°C to 1500°C for pure feldspar compositions. The formation of eutectic melts occurs at lower temperatures, around 990°C for potash feldspar and approximately 1050°C for soda feldspar [71]. The melting temperature of the feldspar was not measured as it is above 1400°C (temperature limit of the machine used).

Table 1.4. Characteristic temperatures.

Samples	T sintering (°C)	T softening (°C)	T sphere (°C)	T semi-sphere (°C)	T melting (°C)
Na-feldspar	1199	1296.1	1329.2	n.a.	n.a.
Lapillus	1132	1181	n. a.	n. a.	1224
Pumice	972	1004	n. a.	1274	1319

The HSM provided information about the characteristic temperatures:

- sintering temperature: temperature at which the sample is reduced by about 5%, the sintering process of the grains begins;
- softening temperature: temperature at which the sample takes on a plastic character, both the upper profile and the edges tend to round off;
- sphere temperature: temperature at which the height is the same size as the width acquiring a spherical shape;
- semi-sphere temperature: temperature at which the width of the sample reaches dimensions twice as large as the height;
- melting temperature: temperature at which the width of the sample is three times its height.

The values obtained are consistent with their use as ceramic fluxes. Pumice is lower melting point than lapillus, and this may be due to the high content of amorphous phase but also to the higher presence of alkaline ions. In both cases, nevertheless, good behaviour in the mixtures can be assumed as the firing T are close to the melting point (for porcelain stoneware $T=1210^{\circ}\text{C}$).

1.6 CONCLUSIONS

The volcanic rocks and processing scraps were characterized in order to evaluate their physico-chemical, microstructural and thermal properties for understanding their possible industrial applications to improve the circularity of production cycles.

From the analyses carried out it can be concluded that:

- due to the lightness of the volcanic products they can be used in the design and preparation of lightweight aggregates useful for agronomic purposes or in the construction field;
- due to the aluminosilicate nature together with the presence of an amorphous fraction pumice and lapillus can play the role of precursor for geopolymer preparation;
- due to the porous nature of zeolitic tuff, it can be exploited for flue gas treatment, being characterized by open structures with high surface areas;

- due to the presence of feldspathic phase (sanidine), pumice and lapillus can be used in the tile's production as fluxes in substitution of natural feldspars,
- for the calcium content lapillus can be used as supplementary cementitious material or as aggregates in the formulation of new OPC mixtures;
- due to the presence of several chemical elements (Si, Al, K, P, Ca), it can be used in the production of fertilizers, either as a carrier or in glass form.

2. PORCELAIN STONEWARE

2.1 STATE OF THE ART

The production process of ceramic tiles is a complex process consisting of several stages, each of which contributes to the quality and characteristics of the final product. The main stages of ceramic production are as follows:

- *Selection and preparation of raw materials.* Raw materials for ceramic production can be natural, semi-processed or synthetic. Natural and semi-processed raw materials are used for substrates and glazes, while synthetic raw materials are used for substrates, glazes, advanced ceramics and process additives. Natural raw materials include clays and kaolin, feldspars, quartz, carbonates and talc; semi-finished materials include glazes, frits and glass while synthetic raw materials include synthetic pigments, additives and oxides. The function of the raw materials is: (i) to provide plasticity and workability to the ceramic piece, this is achieved through the use of clays (ball clays or red clays with varying Fe_2O_3 content) and kaolin (kaolin in the narrow sense, refractory clays with high alumina content and kaolinite rocks with different kaolinite content); (ii) to bring about consolidation by promoting sintering, and this is achieved through feldspars and/or feldspathoids (mainly soda or potassic) and alkaline earth metal oxide systems (e.g. calcite and dolomite); (iii) to functionalize in terms of textural microstructure (quartz, quartz sands, chamotte), aesthetics (e.g. pigments) and functionality (e.g., zircon, corundum, etc.) [72][73]. These materials are selected according to the desired characteristics for the final product and mixed in precise proportions [74].
- *Grinding and refining raw materials to obtain ceramic body.* Raw materials are ground and reduced to very fine powders using ball or hammer mills. This process improves the homogeneity of the mixture and simplifying subsequent processing steps. The ceramic mixture can be obtained in different forms: i) dry, the mixture is granulated for subsequent pressing, the process therefore does not require subsequent atomization and the particle size reduction is less severe; ii) wet, the mixture is mixed with water until a fluid suspension (slip) is obtained, a very severe particle size reduction is required ($\phi < 63 \mu\text{m}$) but on the other hand a better homogenization is obtained [72][75].

- *Atomization of slip.* Atomization is a rapid drying process of suspensions that takes the ground material from a high-water content (37-33% wt) to a much lower value (3-6% wt), suitable for the press forming process. The atomization process yields a semi-finished product consisting of almost spherical agglomerates with high fluidity [72][76].
- *Product forming.* This is done by pressing, which is the production stage in which ceramic products are formed by compacting powders or pastes. During pressing, the following operations are carried out: i) tile forming, which is used to give the semi-finished product a defined geometry, ii) powder compaction, which is used to give the ceramic piece certain physical-mechanical characteristics, iii) powder thickening, which is used to limit voids in the pressed body. The action of compacting and thickening effects of powders are favored by the pressure applied, the plasticity of the mixture, the moisture and the particle size distribution. Pressing affects the final properties of the material, and the objectives are to obtain tiles of a predetermined size without defects and to form a microstructure that has a high bulk density, sufficient raw strength to handle the pieces for subsequent processing, adequate raw permeability and predefined fired properties [77][78].
- *Drying.* After forming, the ceramic products must be subjected to a suitable drying period, the purpose of which is to remove most of the body (interstitial, zeolitic, or constituent) and hygroscopic water they contain. This water must be removed before firing by an appropriate natural or forced drying cycle, depending on the body composition, grain size, water content, shape and thickness of the objects, load density of the dryer, in order to avoid serious deformation and cracking defects. Drying is carried out in facilities (dryers) equipped with heat sources that heat a mass of air in order to increase its evaporative capacity. This invests the product to be processed and increases the surface vapor pressure of the water, allowing it to evaporate [79][80].
- *Firing.* Firing is a heat treatment that gives cohesion to the molded and dried pieces, vitrifies the coating and develops the colors of the decoration. Firing consists of heating the green piece to a predetermined temperature and for a predetermined time, so that chemical and physical transformations can take place that cause the mixture and the vitreous coating, if any, to acquire the properties required by the ceramic product. During firing, the product is consolidated, and porosity is reduced through reactions that lead to the formation of new crystalline phases and the development of a vitreous phase. The types of firing used are double firing and single firing. Double firing consists of a

first step, called biscuit firing, in which the dried piece is fired in a kiln at temperatures between 900 and 1100°C; this stage is followed by glazing, which is followed by a second heating cycle-firing in which the pieces are fired again at higher temperatures (1000 to 1180°C) to set the glaze and obtain the finished product. Double firing is ideal for the production of wall tiles. Single firing, used for the production of stoneware, porcelain and slabs, can be of two types: the first involves firing and treatment at the end of the line, while the second involves glazing before firing and treatment at the end of the line. The maximum firing temperatures are 1190-1220°C for porcelain and slabs, 1150-1180°C for single firing and 1120-1150°C for monoporosa [73][81].

- *Glazing and decoration.* Depending on the type of ceramic, glazes or decorations are applied using screen printing for more complex designs or digital decoration [78][82].
- *Quality control and packing.* After cooling, the products are inspected for defects in shape, color and glaze. Finally, they are packed and shipped[74][77].

This process can vary depending on the type of ceramic (majolica, stoneware, porcelain, terracotta), but the main steps remain the same.

Italy ranks among the world's top ten producers and second in Europe of ceramic tiles with a production of 431 million m² and 374 million m² in 2022 and 2023, respectively; in the latter year, there was a decrease of about 13% compared to the previous year. World production of ceramic tiles in 2021 was about 18 billion m², an increase of about 7% compared to 2020, while in 2023 it decreased by 5.5% to 15,937 million m² from 16,862 million m² in 2022 [83].

The ceramics industry in recent years has been stressed first by the arrival of the pandemic, which caused a forced halt in production, and then by the conflict between Ukraine and Russia, which created problems in the raw material supply chain due to the drastic reduction in clay exports from Ukraine, as well as an uncontrolled increase in natural gas and electricity prices. The ceramics industry is also an energy-intensive sector; therefore, it faces the challenge of reducing emissions in order to comply with the Agenda 2030 sustainable development goals [84].

The production of construction materials, which include ceramic tiles, is among the processes with the largest environmental impact globally and its decarbonization is a goal to be achieved by 2050. The construction sector accounts for about 40% of European energy demand, with 80% of energy derived from fossil fuels. In 2021, it contributed to 37% of global CO₂ emissions

and 34% of global energy demand. In addition to energy consumption and emissions, the sector impacts ecosystems through consumption of land, water and raw materials [85].

It should be borne in mind that the production cycle of Italian ceramics is already structured according to the principles of the circular economy: almost all production and purification waste is reintroduced into the production cycle, about a quarter of raw materials travel by rail, 97% of factories reuse process water and about half of the energy used in production comes from cogeneration or renewable sources [86]. However, the increase in tile production, relative to the year 2021, has necessitated the procurement of an ever-increasing number of raw materials, which are non-renewable resources in the short term and could therefore be exhausted soon.

Based on these considerations, instead of searching for new virgin raw materials, it is preferable to:

- make the process more virtuous by trying to use scraps, waste or by-products of other production processes;
- limit the environmental impacts caused by long-distance transport by favoring local rather than foreign raw materials.

The literature on ceramic tiles is vast and there are several researches based on the addition or substitution of various types of waste within ceramic mixtures for the production of porcelain stoneware. *Conte et al.* studied the technological behaviour of using high percentages of flux substitution with different types of glass waste [87], while *Gualtieri et al.* evaluated the inclusion of high percentages of borosilicate glass waste in stoneware tiles fired at low temperature [88]. Some authors have evaluated the inclusion of sodium-calcium glass scraps in ceramic body [89][90], while other studies in the past have focused on the reuse of glass from the disposal of cathode ray tubes [91]. The inclusion of glass waste is a valid option, but only in small percentages, as the densification process starts at lower temperatures than the reference values and, at high replacement rates, leads to lower sintering efficiency with swelling effects [92]. The addition of these types of waste in ceramic mixtures could not only replace virgin raw materials but also reduce the firing temperature [88][89].

There are also feasibility studies in the scientific literature on the replacement of fluxes with quarry dust from zeolitic rocks, used for their fusibility, low hardness and low cost [93], and with blast furnace slag [94]. Other studies investigate the use of scrap or waste such as incinerator bottom ash and fly ash [95][96][97], foundry sands [98][99], eggshells to replace

limestone [100] and composite materials from industrial plastic waste and recycled nylon fibers to improve the performance of floor tiles [101].

It is still possible to find articles in which the technological properties of ceramic tiles were investigated, in which the clay fraction consisted of iron-rich clays: Italian red clay [102] and Thai red clay [103] for the production of porcelain stoneware, lower quality clays rich in CaO and Fe_2O_3 for the production of high-quality industrial prototypes with reduced firing temperatures [104]. Mixtures have been studied for the production of porcelain stoneware based on Spanish kaolinitic clays after reducing, through physical processes, the impurities of iron compounds and organic matter [105] and based on Colombian kaolinitic clays, introducing different fluxes to increase the degree of sintering [106]. The behaviour of Tunisian plastic clays was compared with that of plastic clays commonly used in Italy for the production of porcelain stoneware [107], but the behaviour of white-fired plastic clays from central and eastern European regions was also studied [108]. In addition, the use of serpentinite waste sludge from dunite quarries as raw materials in the ceramic industry has been evaluated [109], the replacement of part of the clay fraction with bentonites has been studied [110], and the effect of hematitic iron ore and limestone additives on the stiffness of bentonite clay paste materials for porcelain stoneware has been investigated [111].

Although, as mentioned above, the Italian production chain is designed with sustainability as a priority, since 100% of raw and fired waste and water is reintroduced into the production cycle, 47% of energy is self-produced and 99% of dust is filtered [112], and ceramic tile production emits less CO_2 than clinker production, the raw material supply chain must be considered: clinker production facilities are located close to the production sites, while more than 50% of raw materials for ceramic tile production come from abroad by sea, rail or road [113].

The demand for sustainable buildings is growing. However, it is necessary to produce products that are not only environmentally friendly but also have satisfactory technological properties. Life Cycle Assessment (LCA) is a useful tool for understanding and minimizing the environmental impact of products and services. As the world moves towards sustainability, LCA plays a crucial role in assessing and improving environmental performance by enabling the analysis of the environmental impacts associated with all stages of the life of a product, process or service.

The Society of Environmental Toxicology and Chemistry, in 1993 defined LCA as an objective process of assessing the environmental impacts associated with a product, process or activity by

identifying and quantifying material and energy consumption and emissions to the environment and identifying and evaluating opportunities to reduce those impacts. Defining the boundaries of the system is very important as it allows to determine which processes, operations and flows should be considered: there may be several possibilities, for example, cradle to gate, cradle to grave and cradle to cradle. Referring to a product, the cradle-to-grave analysis covers the entire life cycle: from the extraction and processing of raw materials to the production, transportation, and distribution of the product, its use, reuse, and maintenance, to the recycling and final disposal of the product after use. In contrast, in the cradle-to-gate pathway the end of the scope is the factory gate (usually before the product is distributed to customers). It analyzes only up to the point where the product leaves the manufacturing facilities. The latter approach is sometimes preferred when the product can be easily recycled or composted, avoiding landfill, or simply because it is easier to track. ISO 14040 and 14044 provide the framework for conducting LCA studies and define four main steps:

1. goal setting (ISO 14040);
2. inventory analysis (ISO 14041);
3. impact assessment (ISO 14042);
4. interpretation of results (ISO 14043).

Each stage plays a key role in the analysis, enabling a detailed understanding of environmental impacts during the life of a product or service. Its application helps to identify critical areas of environmental improvement, assess the environmental performance of products and services and support decisions in the choice of alternative materials or processes.

Numerous LCAs have been performed on ceramic tiles to assess their ecological footprint. *Vieira et al.* [114] analyzed different works concerning the Brazilian ceramic tile industry identifying the relationships between the variables affecting the forming process and highlighting the areas that need measures to reduce the environmental impact of production. This study found that the transportation of raw materials from quarries to factories is the stage that causes the greatest environmental impact while the glazing of tiles is the main contributor to environmental effects in the studied industries. *Almeida et al.* [115] evaluated the environmental profile of ceramic tiles produced in Portugal through LCA from cradle to grave; the most impactful processes are due to site activities, transportation, power generation and natural gas production. *Tikul* [116] analyzed the impacts caused by the production processes used by small and medium-sized ceramic tile companies in Thailand, observing that small

companies are more energy-intensive and more impactful than medium-sized ones. *Ma et al.* [117] conducted an environmental footprint assessment on China's ceramic tile manufacturing sector through an LCA study and a view of the energy-carbon-water nexus; the greatest impact in this case was direct emissions, energy, transportation, and solid waste. *Morfino et al.* [118] analyzed through LCA the impacts from the use of bleaching materials incorporated within ceramic tile mixtures to provide manufacturers with a tool to guide their choices in the selection of matting materials. *Andreola et al.* [119] and *Barberio et al.* [120] evaluated the environmental impacts of using end-of-life cathode ray tube glass and municipal solid waste incinerator bottom ash for ceramic glaze production and demonstrated the benefits. *Júlia Assumpção de Castro et al.* [121] evaluated the life cycle and environmental contamination of cement tiles while *Türkmen et al.* [122] analyzed different scenarios for tile production to understand which process was more sustainable. Other studies can be found in the literature that use LCA to compare the production of ceramic tiles with marble [123] or to assess the environmental footprint of ceramic floor and wall materials and bricks [124][125][126][127][128]. Moreover, LCA is becoming an increasingly popular tool in the construction industry. In fact, it is possible to find LCAs carried out on different types of mortars, cements and concretes [129][130][131][132][133][134][135][136] and even on aggregates [137][138][139][140].

It must be considered that this methodology has limitations because there is always a tendency to make simplifications of the system when the model is built. This is needed to enable the evaluation of the model itself but could lead to analyses that are not always comparable. If, for example, two different boundaries are considered in the same analysis, a comparison cannot be made. In addition, it is also necessary to consider the type of data such as primary (provided by company), secondary (provided by databases or literature) or tertiary (estimated data). In particular, the latter two increase the uncertainty of the final results. Some studies in literature [141][142] deal exactly with this issue. Further, the country or the time period (or both) can influence the results, therefore they cannot be applicable in a different context. The methods used to analyze impacts are also many, and the analyses obtained by using different methods lead to results that are not comparable to each other.

2.2 PART 1 - REPLACEMENT OF RAW MATERIALS IN COMMERCIAL PORCELAIN STONEWARE MIXTURE: MATERIALS AND METHODS

2.2.1 RAW MATERIALS AND SAMPLES PREPARATION

Due to the characterization performed of pumice and lapillus showing the amorphous fraction content and the presence of alkaline elements, having particle size smaller than 3 mm and supplied by Europomice srl, have been used with the role of substituting the foreign feldspars within a porcelain stoneware body taken as a reference. Changes in the properties of these rocks as a function of temperature allowed them to be considered as fluxes [143]. In addition to volcanic rock scraps, sodium-potassium feldspar scraps from the mining and processing operations of rocks located in quarries present in northern Italy were used.

The plasticity is imparted by the presence of clays, such as: commercial ball clay from central-western Germany (Westerwald region, loc. Meudt), the deposits are of a fluvio-lacustrine environment (dating from the Eocene-Oligocene period) and result from the alteration and erosion of Devonian groves, shales and quartzites; commercial kaolinitic clay from northern Italy (Piedmont region, loc. Novara), the deposits are of a fluvio-lacustrine environment (dating from the Pliocene-Pleistocene); commercial kaolinite from central Italy (Lazio region), originating from kaolinitic deposits formed by hydrothermal alteration phenomena at Quaternary volcanites.

Sands from Emilia-Romagna (Italy), sands from Sardinia (Italy) and raw and fired scraps from the production process were also included in the mixture.

Raw materials were included within the formulations in varying percentages, and the various mixtures were tailored by comparing the resulting chemical and mineralogical analysis with those of the mixture currently in production in the industrial plant. Chemical analyses were performed with an ARL PERFORM'X model sequential X-ray fluorescence (XRF) spectrometer. Mineralogical analyses were performed with an X-ray diffractometer, model X'PERT 3 POWDER PANALYTICAL using the Rietveld method. The quantitative analysis of the crystalline phases was obtained by Rietveld refinements, using GSAS software, and were recalculated based on the absolute mass of the corundum originally added to the mixtures as an internal standard.

All raw materials were dried in an oven at $150^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 4-5 hours to remove moisture. To obtain the samples, the raw materials were mixed with water at a ratio of 1:0.8 or 1:0.45, depending on the target density, and a fluidizer to increase the workability of the mixture has been used. The obtained slip was then dried, ground, and humidified to 6 wt%. After the powders were compacted with a hydraulic press at a pressure of 70-75 MPa to obtain specimens with a diameter of 50 mm for firing (industrial cycle: 48 minutes at 1210°C) and specimens having dimensions of 50 mm x 100 mm were used to determine flexural strength on green. The pressures applied are very high and do not correspond to those applied during production. These pressure values allow for water absorption values comparable to those that would be obtained by direct firing on industrial kiln rollers and not on a refractory plate (the firing mode used for the samples). The prepared formulations can be seen in **Table 2.1**; the abbreviations L and P indicate lapillus-based and pumice-based ceramic bodies, respectively. Concerning the reference sample, it contains a mix of two German clays, a mix of five Italian feldspars, and a mix of six Turkish feldspars (sodium and potash sodium) and other Italian components. The reference consists of 18 raw materials, both Italian and foreign, while the studied formulations are made with 8-10 raw materials of which only one is foreign (German clay).

Table 2.1. Batch prepared using P and L compared with the reference (only for the reference: a=mix of two German clays, b=mix of five Italian feldspars, c=mix of six Turkish feldspars).

	REFERENCE	L1	L2	L3	L4	P1	P2	P3	P4
German clay	35.4% ^a	34%	35%	35%	35%	33%	34%	35%	35%
Italian clay	3.8%	4%	3%	2%	2%	4%	3%	2%	2%
Italian kaolin	9.0%	8%	9%	8%	8%	6%	6%	8%	8%
Lapillus	-	13%	12%	12%	15%	-	-	-	-
Pumice	-	-	-	-	-	13%	15%	15%	16%
Italian feldspar	18.3% ^b	13%	23%	22%	19%	13%	15%	19%	17%
Turkish feldspars mix	24.1% ^c	-	-	-	-	-	-	-	-
Italian sand (Emilia-Romagna)	2.3%	-	-	3%	3%	6%	-	3%	5%
Italian sand (Sardinia)	2.3%	-	-	3%	-	-	-	-	-
Mix scraps	4.9%	15%	-	-	-	12%	12%	-	-
Chamotte	-	13%	18%	15%	18%	13%	15%	18%	17%

2.2.2 SLIP AND GREEN CHARACTERIZATION

The slip was analyzed by evaluating viscosity, density and residual fraction. On the green, permanganate oxidability and flexural strength were evaluated.

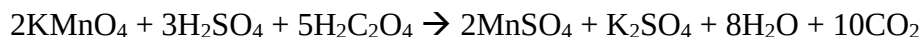
The slip was placed inside a Ford cup with a 4-mm-diameter nozzle, and the time required to empty the cup was measured. The density value was obtained according to Eq. 1, once the weight of the suspension contained in the pycnometer and that of the pycnometer itself were known:

$$d \text{ (Kg/cm}^3\text{)} = (tw - pw)/1000 \quad (1)$$

where: d density, tw total weight (g) and pw is the pycnometer weight (g).

The residual fraction was obtained by passing the slip through a sieve having a mesh diameter of 63 μm and weighing the remaining solid mass on the sieve.

The presence of oxidizable substances within the mixture was evaluated through Kubel's method, an indirect titration method by which the ability of potassium permanganate to oxidize organic matter to CO_2 and H_2O in an acidic environment is analyzed when hot. This analysis makes it possible to assess the possible defects that could be encountered during cooking, such as, for example, the formation of black heart and subsequent swelling due to the presence of numerous oxidizable substances that would need more oxygenation to be flushed out [144]. The reaction that commands this phenomenon is as follows:



Potassium permanganate in the presence of sulfuric acid is reduced to manganous sulfate thus providing elemental oxygen for the oxidation of organic matter. Inside a beaker containing 100 ml of double-distilled water were placed 1 gram of ground sample, 5 ml of 1:3 H_2SO_4 solution and 10 ml of 0.01 M KMnO_4 , and the whole is then brought to a boil for about 10 minutes. After boiling, 10 ml of $\text{H}_2\text{C}_2\text{O}_4$ 0.01 M is placed inside the beaker and potassium permanganate, used as a titrating agent, is added until the color of the solution changes (transparent to rose violet). The result is expressed in mg/l of oxygen consumed, which is derived by multiplying

the milliequivalents of permanganate consumed at the endpoint by the milliequivalent weight of oxygen and then dividing this product by the volume of sample used (0.1 liter) [145].

Flexural strength is a parameter used to evaluate the ability of the tile to resist static and dynamic loads when placed in service. The standard considers the tile as a beam, placed on two rollers spaced apart, while a force is applied in the center by a third roller. The breaking load is the weight that is born before the specimen breaks. Measurement of this parameter on unfired ceramic specimens having dimensions 50 mm x100 mm was carried out with a Gabbrielli Technology mini-CRC 2 Chrometer according to DIN 51030, UNI EN ISO 10545-4. Each measurement was performed on a minimum of 4 samples, and the value reported below is the average of the values of the individual samples. This is a normative parameter when measured on the fired piece, but it is also a very important parameter on the green piece, because it allows us to understand whether the tiles have sufficient mechanical strength to be moved around the plant to pass from one step to another. The instrument consists of a working base, which rests on the sensing element, i.e., the electronic load cell, and houses the associated lower supports. The upper part is motorized and applies and controls the load during the working stroke (constant increment 1 N/mm²s). The breaking stress (S) is obtained by multiplying the breaking load F , i.e., the force applied at the centerline of the working surface, by the ratio L/b (roller distance/tile width). Once F is known, the breaking modulus (σ) can also be calculated according to Eq.2:

$$S (N) = F \cdot L/b \quad (2a)$$

$$\sigma = 3FL/2bh^2 \quad (2b)$$

The standard applies to all types of tiles and porcelain stoneware [146].

2.2.3 FIRED SAMPLES CHARACTERIZATION

On fired samples loss of ignition, linear shrinkage, vacuum water absorption were calculated. In addition, thermal and thermomechanical characterization and colorimetry were carried out.

Loss of ignition (LOI) was calculated according to Equation 3:

$$LOI (\%) = (w_i - w_f)/w_i \cdot 100 \quad (3)$$

where: w_i is the initial weight of the sample, w_f is the weight of the sample after firing.

Linear shrinkage was calculated on fired specimens by measuring with a caliper the dimensional changes of them in five different points to obtain an average value. Equation 4 by which the parameter was calculated is as follows:

$$LS (\%) = (d_i - d_f)/d_i \cdot 100 \quad (4)$$

where: d_i is the initial diameter (50 mm) and d_f is the diameter of the sample after firing.

The fired samples were placed in a laboratory instrument (ISOVACUUM 650, Gabbrielli Technology) to determine vacuum water absorption in ceramic tiles with fully automatic cycles. The vacuum test is carried out as follows: the tiles are placed in a special grid and fed into the tank (made of AISI - 304 stainless steel); then the cycle is started with the vacuum pump. When the required vacuum is reached and maintained, the pump stops. The tank, at this point, fills with demineralized water up to 50 mm above the maximum height of the tiles (adjustable level due to the presence of an electronic sensor). The vacuum regime is discharged, and the tiles remain immersed in the water for the time prescribed by the standard. In this way, apparent porosity, apparent relative density and water absorption can be determined. The instrument has been tested and set to perform ASTM C 373, ISO 10545-3, ISO 10545-12 4.2.6 standards. Once removed from the instrument, the samples were properly dried to remove excess surface water and weighed. The per cent water absorption (WA%) was calculated according to Eq. 5:

$$WA (\%) = (w_f - w_{pf})/w_f \cdot 100 \quad (5)$$

where: w_f is the final weight, w_{pf} is the post-firing weight.

A number of samples were subjected to thermal analysis and compared with reference. The thermal characterization techniques used were thermogravimetric analysis (TG), differential thermal analysis (DTA), optical and mechanical dilatometry.

Differential thermal analysis was performed on the mixtures by a simultaneous thermal analyzer NETZSCH STA 429 (CD). The samples were ground to an impalpable powder (average particle diameter less than 20 µm), and the analysis was carried out at a heating rate of 10°C/min (see *section 1.4.2*).

The optical dilatometer is an instrument used to study the sintering of ceramic bodies and their thermal stability range while avoiding the risk of swelling by providing sample expansion (%) as a function of temperature as a result. Using optical technology, the best firing cycle can be determined without risking damage to the material. The measurement was performed with the Expert system ODHT-HSM solution mod. M3MD 1600/80, at a maximum temperature of 1280°C and a heating rate of 10°C/min, on unfired solid samples prepared with a height of 15 mm, and with 5x5 mm edges. All samples were dried in an oven at 105±5°C overnight and stored in a desiccator before use.

The mechanical dilatometer was used to measure the thermal expansion of the specimens to obtain the Linear Thermal Expansion Coefficient (α). The fired samples, having a length of 38 to 50 mm, were subjected to a constant negligible mechanical load and simultaneously to a controlled temperature/time program. Measurements were made with a MECHANICAL DILATOMETER, Netzsch Dilatometer 402 EP, with a heating rate of 5°C /min setting a maximum temperature of 600°C.

In order to determine the effect of the addition of pumice or lapillus on aesthetic properties, fired samples were analyzed using a UV-vis spectrophotometer (SPECTROPHOTOMETER CM-2600d, KONIKA MINOLTA), which operates in the CIE L*a*b* color space, allowing the set of colors perceived by the human eye to be described.

This analysis was performed by comparison between the best fired samples and the reference. For each sample, five measurements were taken at different points of the surface to analyze any color variations, given by the ΔE^* parameter according to Eq. 6:

$$\Delta E^* = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} \quad (6)$$

If $\Delta E^* < 1$ two colors are not discriminable by convention.

2.3 PART 2 - REPLACEMENT OF GERMAN CLAY WITH ITALIAN ONE IN PORCELAIN STONEWARE MIXTURE: MATERIALS AND METHODS

2.3.1 RAW MATERIALS AND SAMPLES PREPARATION

The raw materials used are described in *section 2.2.1*.

The raw materials described were included in different proportions in the mixture according to their function: 45% by weight of plastic component, about 35% by weight of flow component and about 20% by weight of inert component. The formulations taken as reference, reported as L0 and P0 in **Table 2.2**, correspond to L4 and P4 (**Table 2.1**, *section 2.2.1*). From these formulations, German clay was gradually replaced by 25%, 50% and 100% Italian kaolinitic clay to assess the influence on the technological properties as the substitution rate increased. The batches differed between them in the presence of lapillus or pumice rock, so for simplicity we will refer to the products made from lapillus or pumice rock. The two clays were characterized chemically, mineralogically and thermally. The chemical and mineralogical characterisation of the different raw materials was carried out and provided by the producers of these raw materials.

The thermal behavior of the clays was evaluated in terms of reactivity and weight variation with increasing temperature using differential thermal and thermogravimetric analysis. TGA/DTA analyses were performed with a NETZSCH STA 429 CD simultaneous thermal analyzer. The analysis was performed at a heating rate of 10°C/min on ground samples with average particle diameters less than 20 µm.

The formulations prepared can be seen in **Table 2.2**. The letters L and P designate the lapillus-based or pumice-based mixtures respectively, the following numbers indicate the percentage of substitution of German ball clay in favor of Italian kaolinitic clay (e.g. L25 indicates a mix containing volcanic lapillus scraps with 25 wt% of Italian kaolinitic clay and 75 wt% of German ball clay, the percentages calculated refer to the clay component only).

Table 2.2. Batch prepared with pumice-based or lapillus-based bodies by replacing German ball clay with Italian kaolinitic clay. All values are in percentages (%). Please note that the designations are different from **Table 2.1**: German ball clay and Italian kaolinitic clay are German clay and Italian clay, respectively, while chamotte considers both mix scraps and chamotte.

	L0	L25	L50	L100	P0	P25	P50	P100
German ball clay	35	26	17.5	-	35	26	17.5	-
Italian kaolinitic clay	2	11	19.5	37	2	11	19.5	37
Italian kaolin	8	8	8	8	8	8	8	8
Lapillus	15	15	15	15	-	-	-	-
Pumice	-	-	-	-	16	16	16	16
Italian feldspar	19	19	19	19	17	17	17	17
Italian sand	3	3	3	3	5	5	5	5
Chamotte	18	18	18	18	17	17	17	17

Before further testing, all raw materials have been treated as described in *section 2.2.1*.

2.3.2 SLIP AND GREEN CHARACTERIZATION

Slip was analyzed by evaluating viscosity, density and residual fraction, while on green it was performed flexural strength as described in *section 2.2.2*.

2.3.3 FIRED SAMPLES CHARACTERIZATION

On fired samples loss of ignition, linear shrinkage, vacuum water absorption was calculated as described in *section 2.2.3*. In addition, mineralogical, microstructural and colorimetric analysis were carried out.

Mineralogical analysis was performed on the clays and the fired samples in order to assess whether or not new crystalline phases were formed as a function of the amount of Italian kaolinitic clay substituted compared to those found in the samples containing German ball clay taken as reference. The patterns have been recorded on the powdered samples (<38 µm in size)

for the clays and entire for the fired samples (specimen length 10.00 mm) in the 5–70° 2 θ range (step size 0.013° and 1 s counting time for each step), operating at 40 mA and 40 kV mA at room temperature. The measures were conducted using an X-ray diffractometer from PANALYTICAL model Empyrean, with Ni-filtered Cu K α radiation using brackets holder. The identification of the crystalline phases occurred using as software Highscore Plus software version 3.0.

Microstructural investigation was performed in order to evaluate the effect of the replacement of German ball clay with Italian red one. The instrument used is an environmental scanning electron microscope (ESEM-Quanta 200), combined with an X-ray EDS microanalysis system (X-EDS Oxford INCA-350). The fired samples analyzed were reduced to appropriate size (less than 1 cm per side) and were metallized with a gold layer of a few nanometers to make the sample conductive.

Colorimetry was described in *section 2.2.3*.

2.4 PART 3 - LIFE CYCLE ANALYSIS: METHODS

2.4.1 LCA METHODOLOGY

The comparative environmental assessment was performed on the final products described in *Part 1 (section 2.2 and related subsection)* according to the international regulatory reference for the execution of LCA studies represented by the ISO 14040 series of standards. The structure of LCA is divided into four main steps: objective and scope, life cycle inventory, impact assessment and interpretation of results [147].

2.4.2 GOAL OF THE STUDY

The focus was to compare the environmental impacts of a commercial porcelain stoneware with two similar products containing mining and processing scraps of Italian volcanic minerals. The products considered have been engineered within a research and development cooperation between the academic and business worlds. The products have been technologically compared by the authors in [148]. With the results that will be exposed in this work, the authors wanted to complete analysis by evaluating the environmental impact of the product with a view to

promoting commercial and productive transferability, in the context of the circular economy and national productive self-sufficiency.

The products under study were a reference porcelain stoneware produced by a ceramic company that is part of the Sassuolo (MO) ceramic district (Italy), a porcelain stoneware containing pumice scraps and one containing lapillus scraps.

The raw materials used for the production of the samples under studies were described in *section 2.2.1*.

The number of raw materials required to manufacture the product was reduced from 18 to 8. This led to a reduction in dye pigments while achieving good technological properties, as demonstrated in [148].

2.4.3 FUNCTIONAL UNIT AND SYSTEM BOUNDARIES

The studied system corresponds to stoneware tile. Therefore, its function is to provide coverage to the floor of a building. The chosen functional unit is 1 m² of tiles.

The LCA was carried out following a cradle-to-gate approach. The life cycle analysis was evaluated by several stages:

- Raw materials: in this phase, all materials needed to obtain support, engobe and glaze were considered. Processing scraps used as raw materials were considered to have neutral impact since they are not extracted specifically for the purpose. German and Italian clays, Italian kaolin, Italian and Turkish feldspars, pumice scraps, lapillus scraps and Italian feldspar scraps, Italian sands, scraps from the production cycle and dyes of various kinds were used to obtain ceramic support. Clays from Britain and Germany, German bentonites, German sands, Italian feldspars, northern European feldspathoids and ceramic frits from Spain were used to make engobes and glazes. In 2022, 347.5 tons of raw materials have been consumed in the reference plant for the production of reference support only;
- Transportation: transportation of all raw materials from the respective quarries/mines to the production plant was considered in this phase. The routes were traveled by road, train, and sea. The distance traveled by road, to get from the quarries to the production plant, can be very different; there are local raw materials that travel about 12 km but there are also raw materials that come from abroad traveling about 1200 km. The same

for transportation by sea, as Italian raw materials travel about 280 km while foreign raw materials can travel up to about 8050 km. Only one raw material, German clay, travels by train, so the distance is constant corresponding to 900 km;

- Production: this phase accounts for all the processes required to obtain the products with the related energy consumption and emissions generated to complete the process. The energy consumption considered in this phase also includes the packaging phase. The production is related to the manufacture of approximately 6.255.444 m² of porcelain stoneware produced in 2022 (considering that 18 kg of raw materials related to the substrate only are used for 1 m²). In all cases studied, the considered firing cycle is the one currently used by the company, i.e. a time of 48 minutes at a temperature of 1210°C.

The scenarios considered in this investigation were:

- Reference porcelain stoneware scenario (REFERENCE), which describes the sourcing and transportation of raw materials to the factory and the production of the product considered;
- Scenario of porcelain stoneware containing 16% of pumice scraps (PUMICE-BASED), which in addition to accounting for sourcing, transportation, and manufacturing of the product, goes on to consider the non-extraction of some raw materials and the decrease in the use of coloring oxides (approx. 50%);
- Scenario of porcelain stoneware containing 15% of volcanic lapillus scraps (LAPILLUS-BASED), which contains less sand and more feldspars than the previous one [148].

PUMICE-BASED and LAPILLUS-BASED refer to P4 and L4 respectively (see **Table 2.1** in *section 2.2.1*).

Figure 2.1 summarizes the life cycle stages considered; these are the same for all three scenarios.

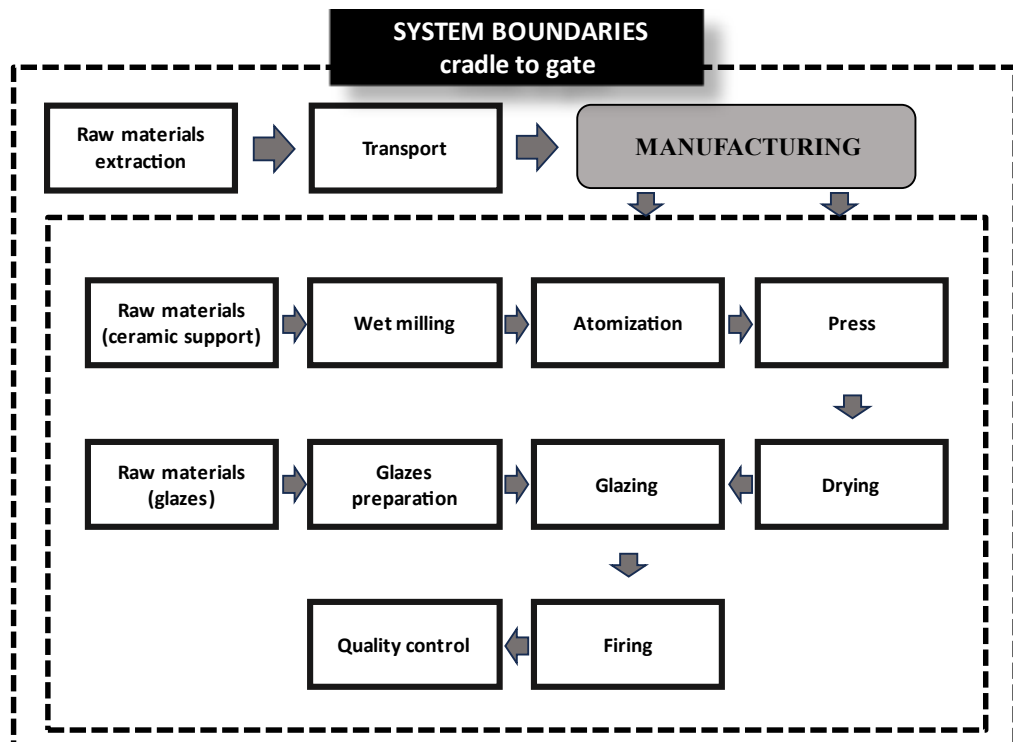


Figure 2.1. System boundaries.

2.4.4 ASSUMPTIONS AND CONSIDERATIONS

The following assumptions were made for each scenario:

1. The amount of mix to obtain 1 m² of tile is 18 kg [149];
2. The selected means of transportation were those with lower emission levels (Euro 6 certified trucks, electric-powered trains). These were chosen in the absence of information because they comply with European emission reduction regulations, which are stricter than the previous Euro 5 standards;
3. The coloring oxides used to color the substrate are reduced by 50% in the case of pumice-based and lapillus-based mixture, as they naturally color the ceramic piece (brown for pumice-based, black for lapillus-based);
4. All raw and fired waste is fed back into the production cycle.

Since there is no direct or good quality data, nor high interest because they are the same in all scenarios, the following parameters were not considered within the process:

1. Emissions related to dust and fume removal systems (SolirocTM process [150]);
2. Waste production and disposal (for example insulators);

3. Water consumption, as this is recycled within the production cycle [151];
4. Energy produced in cogeneration;
5. Fuels used for vehicles loading hoppers.

2.4.5 LIFE CYCLE INVENTORY ANALYSIS

Life cycle inventory analysis is a phase that includes the collecting and processing of data on all inputs and outputs of the production system under consideration. In order to obtain a valid model, the inventory must be as complete as possible.

Data on raw material extraction and transportation (not km traveled but related to fuels, emissions, ecc...) come from the Ecoinvent v3 database [152][153]. In this regard, the data on the processes that most closely resemble the objective and scope of this study were selected, with a global scope and sintering temperatures similar to those used in this life cycle study; data on transportation (km traveled), quantities of raw materials used, and energy consumption were primary data, i.e., provided directly by the tile maker company involved in this study.

Data on the quantities (kg) of raw materials needed for the annual production of porcelain stoneware were provided by the manufacturing company. Carriers deliver the raw materials needed for production every week; upon entering the company these are mandatory to declare the quantities delivered, which are then certified by the operators. The quantities are recorded and make it possible to obtain very reliable estimates of the raw materials purchased and used. The unit of measurement related to the quantities of raw materials was “kg”.

Raw material transport data, on the other hand, were provided by the mining companies. Distances were estimated on the basis of actual kilometers traveled by transporters (in the case of road routes), trains or ships. However, the data were checked and confirmed through the use of high-accuracy maps. The unit of measurement related to transportation was “tkm” (ton per km).

Regarding energy data, it must be considered that ceramic companies, being highly energy-intensive companies, are subject to mandatory energy diagnosis in accordance with Legislative Decree 102/2014. Energy diagnosis is defined as a procedure aimed at providing adequate knowledge of the energy consumption profile of industrial plant. Thus, diagnosis is the most qualified tool for analyzing the energy management framework of an activity: it highlights the

level of management efficiency, starting from the analysis of significant energy flows, to identify the most energy-intensive process steps and machines.

Electrical and thermal equipment consumption data were collected or calculated by:

- Field measurements of consumption (continuous meters, periodic readings of parameters for industrial management/accounting, ecc...);
- Spot readings of consumption by instrumentation inserted for periods deemed significant to the interpretation of the consumption trend of the equipment under consideration;
- Estimation of consumption based on nameplate powers, time of use of the equipment and the sensitivity of the department head in defining possible correction factors (average power consumed versus nameplate power).

In this case, for electricity consumption, the company has tax counters for purchase and production (co-generator); a tax counter also measures the consumption of natural gas taken from the pipeline.

The company in 2023 carried out the energy diagnosis, and the expert staff who dealt with it validated the data reported in this paper. However, all data were rechecked to be sure of the quality of the input data and consequently have reliable output data. The unit of measurement related to energy was “kWh” and “Sm³” (Standard cubic meter).

Figure 2.2 shows some inventory data for raw material, transportation and energy. It shows the quantities of raw materials needed to produce 1 m² of product and the distances traveled from the quarries to the factory. In terms of distances, the raw materials marked with an asterisk (*) are transported by road and rail, those marked with two asterisks (**) are transported by road, by rail and by sea, and all others are transported by road. "Mix feldspars scraps" means the sum of pumice or lapillus scraps and Italian feldspar scraps.

Regarding the data on the consumption of electricity (kWh) and natural gas (Sm³) needed to produce 1 m² of product (data provided by the ceramic company), they are again visible in **Figure 2.2**. Consumption was considered to be the same for every type of porcelain stoneware. The figure does not show consumption data for auxiliary and general services, which are 0.99 kWh and 0.06 Sm³ and 0.06 kWh and 0.004 Sm³, respectively.

For simplicity of visualization, the merged data have been shown in **Figure 2.2**. As mentioned in *section 2.4.3*, in the case of both quantities and transports, when it comes to clays, it must be

considered that we are dealing with 4 types of them in the case of reference and 3 in the other two cases while, in the case of feldspars, 11 were considered for the reference and 2 (mix feldspars scraps) in the other two scenarios. The sands included in the slurries were 2 in the reference scenario and 1 in the other two cases while for chamotte 1 type was used in the reference and 2 types for the pumice based or lapillus-based scenarios.

Energy data have also been merged; the data visible in the Figure below refer to the sum of the data from the departments considered. For example, the grinding department refers not only to the operation of grinding raw materials, but to all the machinery that contributes to this stage: conveyor belts, automatic loading and unloading of raw materials, monitoring booths; the atomization department considers the stage of mixing raw materials with water, sieving, etc...

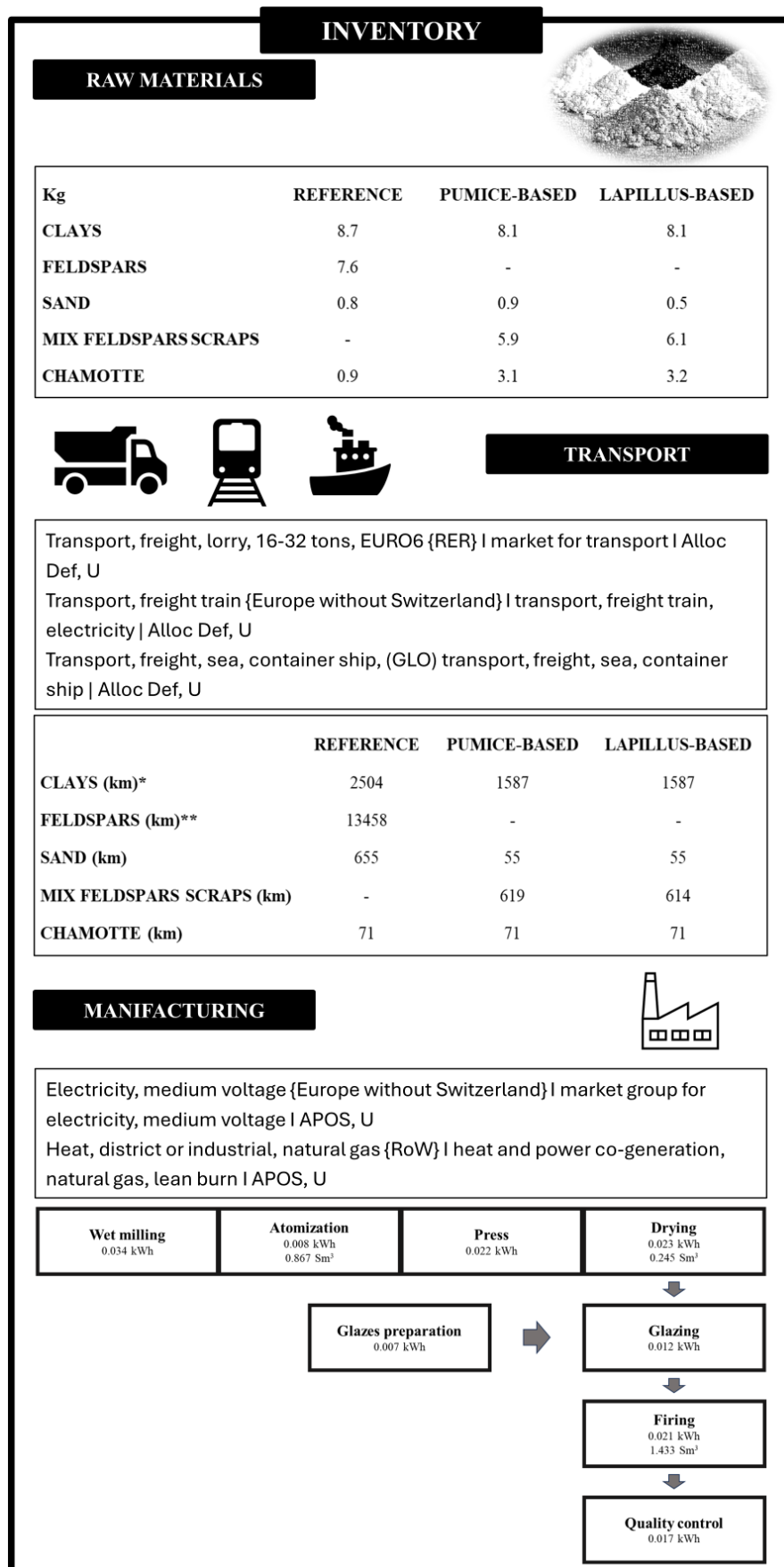


Figure 2.2. Inventory data on (i) raw materials used to obtain ceramic bodies, (ii) transportation of raw materials from quarries to the ceramic plant, and (iii) electricity and natural gas used to produce final products.

2.4.6 LIFE CYCLE IMPACT ASSESSMENT METHODOLOGY

The used impact assessment methodology is CML 2000 version 2.05, developed by Centre for Environmental Studies (CML), Leiden University (Netherlands) in 2001, replacing the CML 1992 method. CML-IA is a database that contains characterization factors for life cycle impact assessment (LCIA) [154]. This methodology allows the following impact categories to be analyzed: Abiotic Depletion, Acidification, Eutrophication, Global Warming Potential, Ozone Layer Depletion, Human Toxicity, Freshwater Aquatic Ecotoxicity, Marine and Terrestrial Aquatic Ecotoxicity, and Photochemical Oxidation. The validity of the results is global in scope, but the Acidification and Photochemical Oxidation categories are based on average values for the European region [155].

This methodology provides information on human health, natural resources and the environment and has been used in numerous works in literature [156][157][158][159]. The evaluation of impact indices against an average European in one year is standardized.

The software SimaPro 8.3.0.0 (PRé Consultants) enabled the model construction and data processing.

2.5 PART 1 - REPLACEMENT OF RAW MATERIALS IN COMMERCIAL PORCELAIN STONEWARE MIXTURE: RESULTS AND DISCUSSION

2.5.1 CHEMICAL AND MINERALOGICAL ANALYSIS OF MIXTURES

Chemical and mineralogical analyses were performed on the raw materials and were provided by the partner companies, as mentioned above. The analyses on the mixtures reported below were not performed by spectroscopic analysis, but by calculating the percentages of the elements and crystalline phases based on the percentage of raw material in the mixture.

The formulations were selected on the basis of chemical and mineralogical similarity of the samples to the reference. The comparison of the chemical and mineralogical analyses can be seen in **Table 2.3** and **Table 2.4**, respectively.

When comparing the chemical analyses, the samples containing lapillus have similar percentages of silica and alumina to the reference, with the exception of sample L2. The

percentage of titanium oxide is similar to the reference. The content of iron oxide is almost double that of the reference, except for sample L4, which has a higher percentage value; in this case it is an added value because it gives a darker color than the reference (naturally colored support). CaO, MgO and K₂O are present in larger amounts than the reference while Na₂O is present in smaller amounts. As for the pumice-based samples, the amounts of silica and alumina are found to be remarkably similar to those of reference in all the formulations studied. The titanium oxide content is practically the same as the reference; therefore, it does not affect the coloration of the ceramic piece, while iron oxide has intermediate percentages between the reference and the lapillus-based slurry; in fact, it takes on an intermediate coloration visible in **Figure 2.3**. Again, CaO and K₂O are present in larger amounts while MgO and Na₂O vary and are present in smaller percentages.

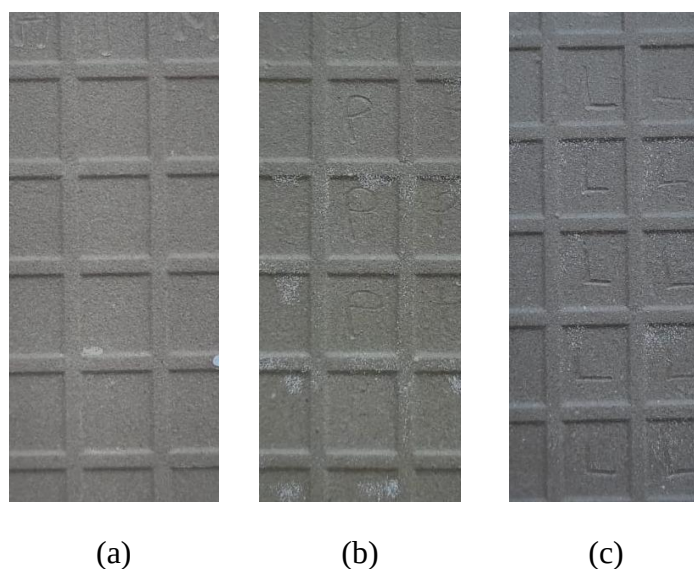


Figure 2.3. Color variation in different mixtures: (a) is the reference, (b) is a pumice sample, and (c) is a lapillus sample.

An interesting ratio is that of silica/alumina, which turns out to be identical to the reference in sample L4 and P2 and very similar in the other samples except L3.

Figure 2.4 displays the different percentages of oxides. It is possible to see a decrease in alkaline oxides and an increase in alkaline-earth oxides. The ratio between alkali and alkaline-earth oxides drops significantly especially in P4. Alkaline-earth oxides help sintering by reducing temperature, so increasing their percentages improves the sintering process by affecting properties such as: shrinkage, water absorption and flexural strength.

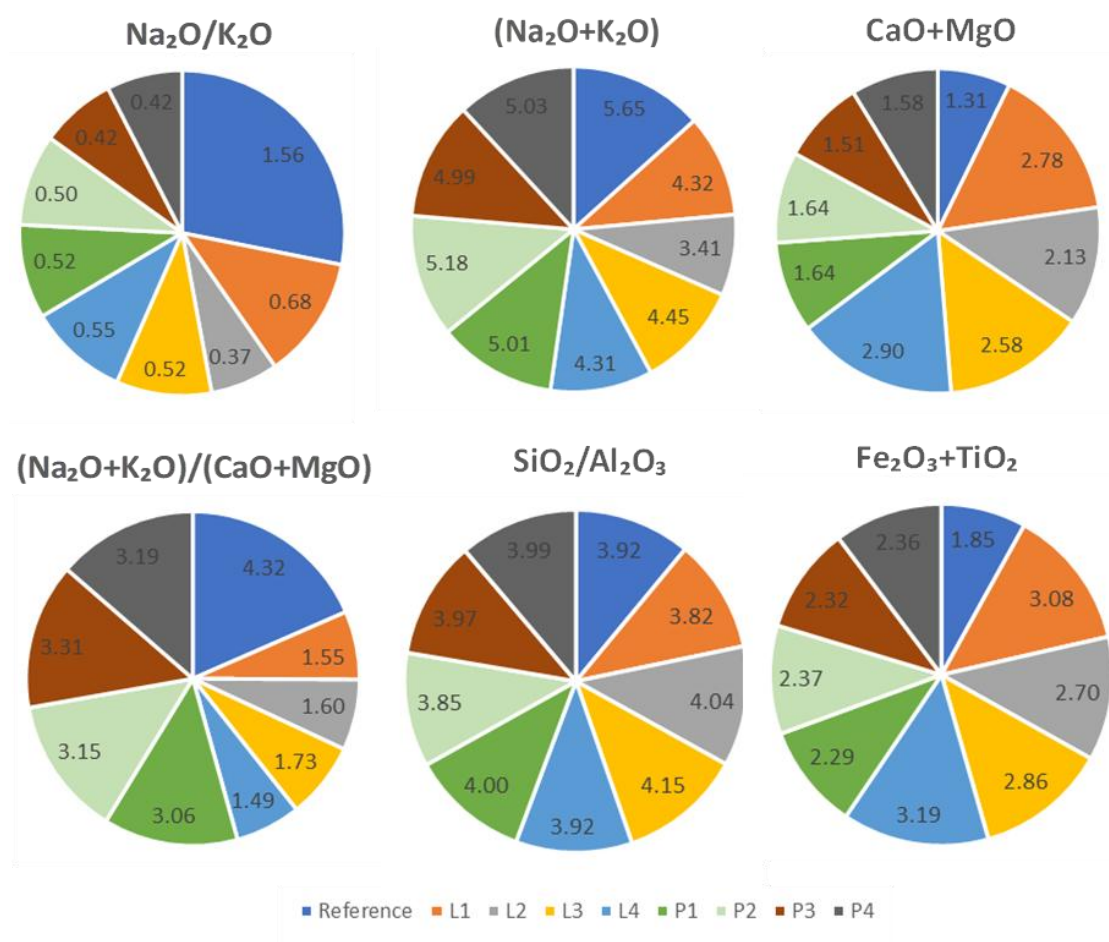


Figure 2.4. Different percentages of oxides in the reference and formulations studied.

Table 2.3. Theoretical chemical analysis of the formulations studied.

	Reference	L1	L2	L3	L4	P1	P2	P3	P4
SiO ₂	69.7	68.2	58.7	69.6	68.4	69.6	68.8	69.5	69.4
Al ₂ O ₃	17.8	17.8	14.5	16.7	17.5	17.4	17.9	17.5	17.4
Fe ₂ O ₃	1.2	2.3	2.1	2.2	2.4	1.6	1.7	1.7	1.7
TiO ₂	0.7	0.8	0.7	0.7	0.8	0.7	0.7	0.7	0.7
CaO	0.6	1.9	1.4	1.7	2.0	1.1	1.1	1.0	1.1
MgO	0.7	0.9	0.7	0.8	1.0	0.5	0.5	0.5	0.5
K ₂ O	2.2	2.6	2.5	2.9	2.8	3.3	3.4	3.5	3.6
Na ₂ O	3.4	1.7	0.9	1.5	1.5	1.7	1.7	1.5	1.5
Others	3.7	3.8	18.5	3.8	3.8	4.1	4.1	4.2	4.3

Mineralogical analysis shows that samples L4, P3 and P4 have about the same quartz content compared to the reference, the percentage of kaolinite is found to be a bit lower for all samples except L1 where it increases slightly. The illite/mica content decreases in all samples and no sample have montmorillonite content, except L3. In general, the percentage of clay component decreases. The percentages of albite and plagioclase are found to be significantly lower than in the reference while the percentages of orthoclase increase in all samples.

The mineralogical analysis, unlike the chemical one, shows very different crystalline phases, and it can be seen that there are extremely high percentages of unreported phases in all the mixtures studied unlike the mixture taken as the reference.

The very high percentages in the samples containing pumice are mainly due to the percentage of amorphous fraction detected in the pumice (about 80%), while in the samples containing lapillus it is due not only to the amorphous fraction but also to the presence of hematite, which were not considered in the comparison with the reference. In this context, only the mineralogical phases relating to clay minerals and feldspars were evaluated.

Table 2.4. Theoretical mineralogical analysis of the formulations studied.

	Reference	L1	L2	L3	L4	P1	P2	P3	P4
Quartz	30.7	29.8	31.7	32.8	30.4	30.6	28.3	30.5	30.5
Kaolinite	15.6	16.1	15.0	14.6	14.6	15.0	14.9	14.6	14.6
Illite/Mica	11.8	10.5	8.4	8.4	8.4	10.1	10.3	8.7	8.8
Montmorillonite	0.3	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0
Albite	23.3	5.9	5.1	5.4	4.8	6.4	5.7	4.8	4.7
Orthoclase	5.6	8.0	9.3	10.1	9.1	7.3	7.4	7.8	7.5
Plagioclase	8.1	3.4	1.6	1.6	1.6	2.8	2.5	1.2	1.2
Other or not reported	4.7	26.4	28.9	27.0	31.3	27.7	30.8	32.5	32.7

2.5.2 CHARACTERIZATION OF UNFIRED SAMPLES

Figure 2.5 and **Table 2.5** show the values of the parameters analyzed on the slips and unfired sample.

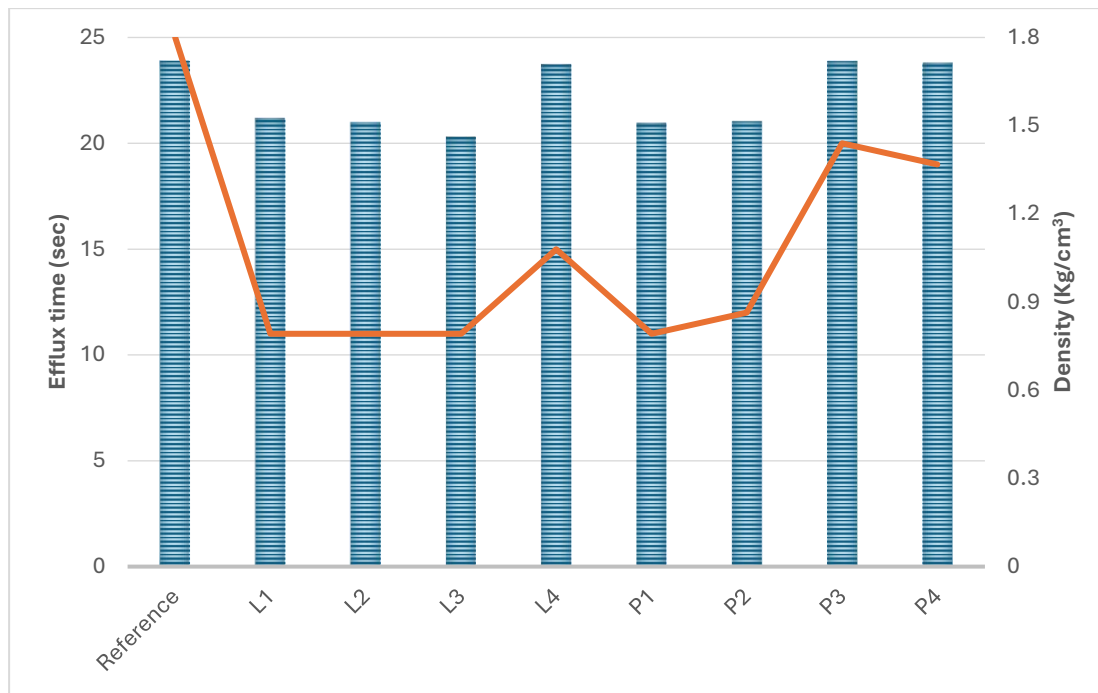


Figure 2.5. Effect of efflux time variation as a function of density. The efflux time is described by the orange line, while the blue columns identify the density values.

Table 2.5. Residual fraction, oxidizable substances and flexural strength.

	Refe rence	L1	L2	L3	L4	P1	P2	P3	P4
Residual fraction (g)	3.5- 4.5	2.29±0. 05	1.94±0. 05	0.28±0. 05	3.75±0. 05	2.22±0. 05	1.82±0. 05	3.12±0. 05	3.72±0. 05
Oxidizabl e substance s (mg/L)	<1	0.47±0. 05	0.63±0. 05	0.63±0. 05	0.63±0. 05	0.57±0. 05	0.60±0. 05	0.63±0. 05	0.63±0. 05
Flexural strength (MPa)	35-50	55.37±0 .5	42.52±0 .5	40.48±0 .5	37±0.5	52.23±0 .5	35.54±0 .5	32±0.5	45.63±0 .5

The results of the measurements show quite similar values of efflux time (**Figure 2.5**) working at low densities (1.4-1.5 Kg/cm³) in the case of both lapillus-based and pumice-based samples. As density increases, moving closer to the value of the reference, there is an increase in the efflux time, and this is due to higher viscosity of the slip as there is more solid loading and less

water. If the efflux time value of the reference is compared with samples L4, P3 and P4, which have similar densities to the standard, it can be seen that its value is much lower in the sample containing lapillus than in the one containing pumice. The latter has efflux time values comparable to those of the standard while the lapillus-containing sample has lower values; this could allow, for the same fluidizer, a decrease in the amount of water required for slip preparation in favor of solid loading or use a lower amount of deflocculating agent.

The residual fraction was measured because it represents an important process parameter, as it allows an assessment of whether the grinding time of the mixture is adequate. The results reported for L4, P3 and P4 are very similar to those of the reference while the other samples presented much lower values. The difference can be attributed to the fact that the above samples were ground for 7 minutes while the remaining samples were ground for 9 minutes. It can be assumed that a grinding time of 9 minutes appears to be too long.

Regarding the presence of oxidizable substances in all samples, the values obtained were adequate and lower than the maximum limit imposed on the reference. Excessive presence of oxidizable substances could lead to the swelling of the ceramic piece due to the incomplete degassing of the organic products that burn turning into gas.

Flexural strength is measured because the tiles during transportation and processing are subjected to stresses. The lowest strengths were recorded in samples L4, P2 and P3. If these values were relative to the fired product, L4 and P2 would still have acceptable values, while P3 would not, as the minimum value required by the standard must be 35 MPa. The values measured on dried bodies agree with the literature [110]. One consideration that can be made is that, in general, the modulus of rupture tends to increase as the porosity decreases so the lower the water absorption, the lower the porosity and the higher the flexural strength of the tile. It should be considered that flexural strength, porosity, water absorption, and shrinkage during firing are parameters that could also depend on the number of alkaline-earth oxides as shown in some works in the literature, from which it was found that the extent of these properties depended precisely on the amount of CaO and MgO [160][161]. P3 presented a higher absorption value and consequently its flexural strength decreased. In the other samples, the value obtained is quite good. The results obtained are consistent with the percentages of alkali-earth oxides in the various formulations, as shown in **Figure 2.4**.

The optimized mixtures result to be L4 and P4, therefore the thermal characterization was performed on these formulations only. **Figure 2.6**, **Figure 2.7** and **Figure 2.8** describe the TG

(red curve) and DTA (blue curve) with thermograms showing peaks, endothermic or exothermic, and weight change of the material under test.

Figure 2.6 describes the behavior of the standard as temperature increases. TG shows a not very high mass loss (4.06%), and the greatest loss occurs between 400°C and 700°C. From the DTA it can be seen that:

- Up to about 150°C, there is a loss of adsorbed water and crystallization;
- Between 370°C and 479°C, dihydroxylation of the clay component occurs;
- At about 570°C the endothermic peak could be associated with the transformation of kaolinite to metakaolin;
- At 980°C, on the other hand, an exothermic peak probably related to the crystallization of mullite, or alumina occurs;
- around 1200°C, an endothermic peak occurs due to the melting of the crystal lattice that makes up the material.

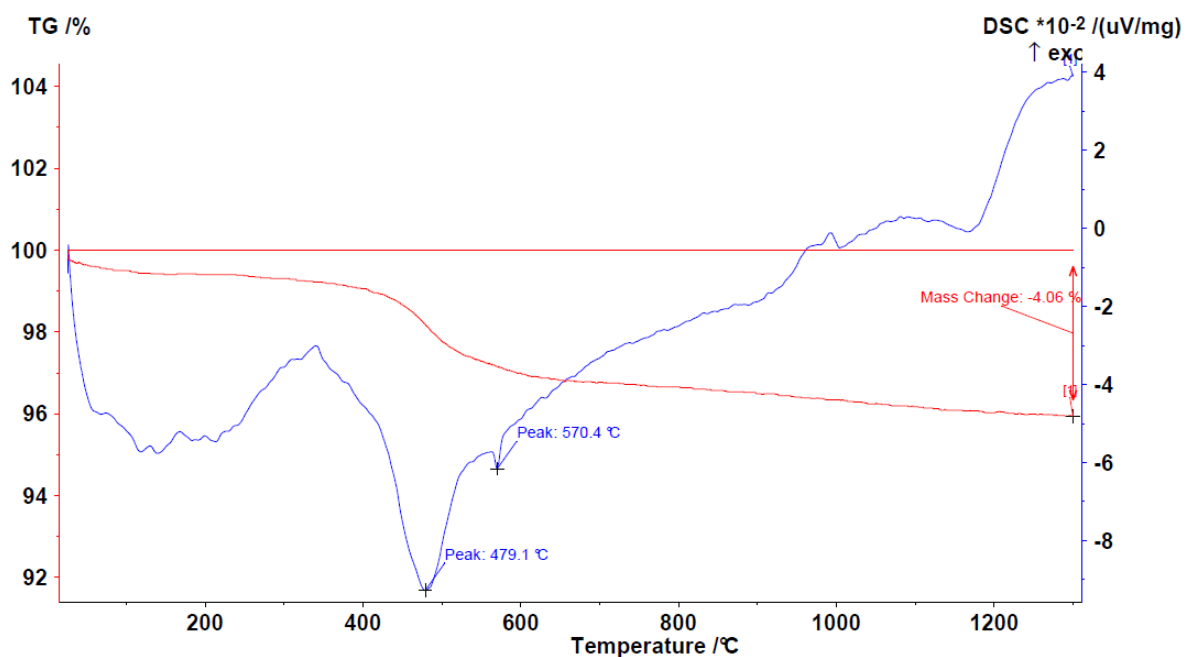


Figure 2.6. TG/DSC reference body.

Figure 2.7 describes the behavior of the sample containing lapillus. TG shows greater mass loss than the standard (6.14%), and the greatest loss occurs up to 600°C. DTA shows that:

- Up to about 120°C there is loss of adsorbed water and crystallization;
- Between 390°C and 507.5°C dihydroxylation of the clay component occurs;
- At around 571°C the endothermic peak could be associated with the transformation of kaolinite to metakaolin;
- around 1150°C an endothermic peak occurs due to the melting of the crystal lattice that makes up the material.

Comparing the lapillus-containing sample with the reference one, it can be stated that: the dihydroxylation of the clay component in the lapillus-based sample begins at higher temperatures; the peak at around 570°C occurs at about the same temperature; the melting of the crystal lattice in L4 sample occurs at lower temperatures than in the reference.

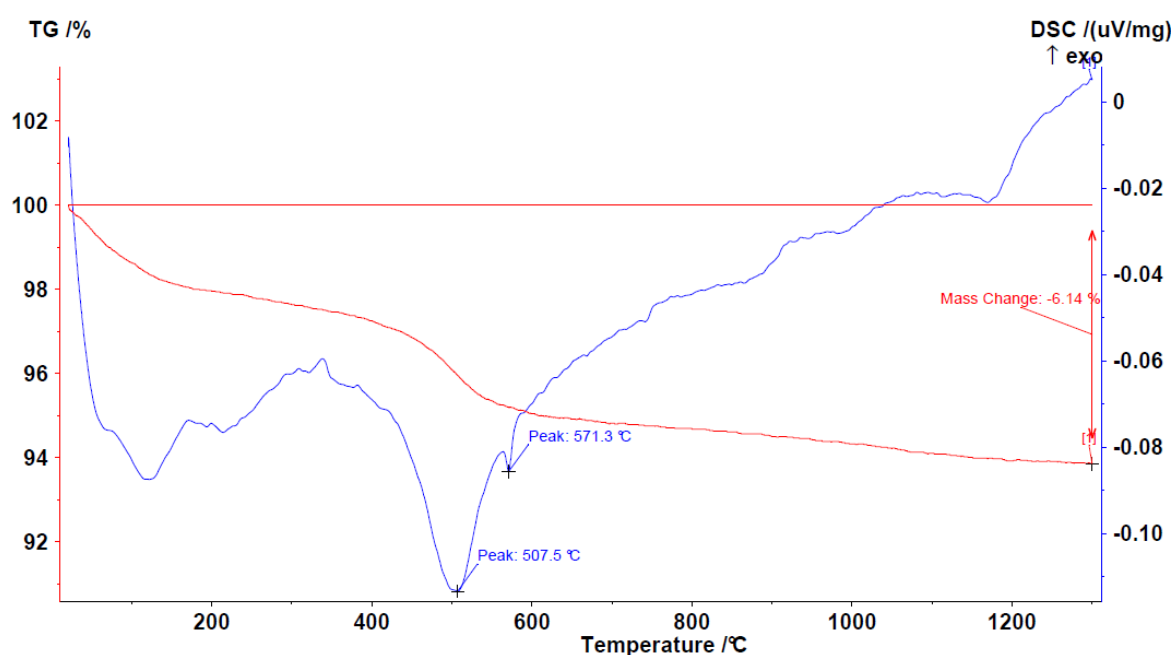


Figure 2.7. TG/DSC lapillus-based sample (L4).

Figure 2.8 shows the thermal behavior of the mix containing pumice. TG shows a higher mass loss (6.78%) than the other two samples, and the highest loss occurs between 200°C and 500°C. DTA allows us to say that:

- Up to about 100°C, there is a loss of adsorbed water and crystallization;
- Between 380°C and 500°C, dihydroxylation of the clay component occurs;
- At around 570 °C, the endothermic peak could be associated with the transformation of kaolinite to metakaolin;
- around 1150 °C, an endothermic peak occurs due to the melting of the crystal lattice that makes up the material.

When comparing the pumice-based mixture with the other two, it is possible to say that the sample has intermediate thermal characteristics between them. The dihydroxylation of the clay component in the pumice-containing sample begins at temperatures higher than the reference but lower than in the lapillus-based sample; the endothermic peak at about 570°C occurs at about the same temperature for all samples while the melting of the crystal lattice in the L4 and P4 samples occurs at about similar temperatures but lower than the reference.

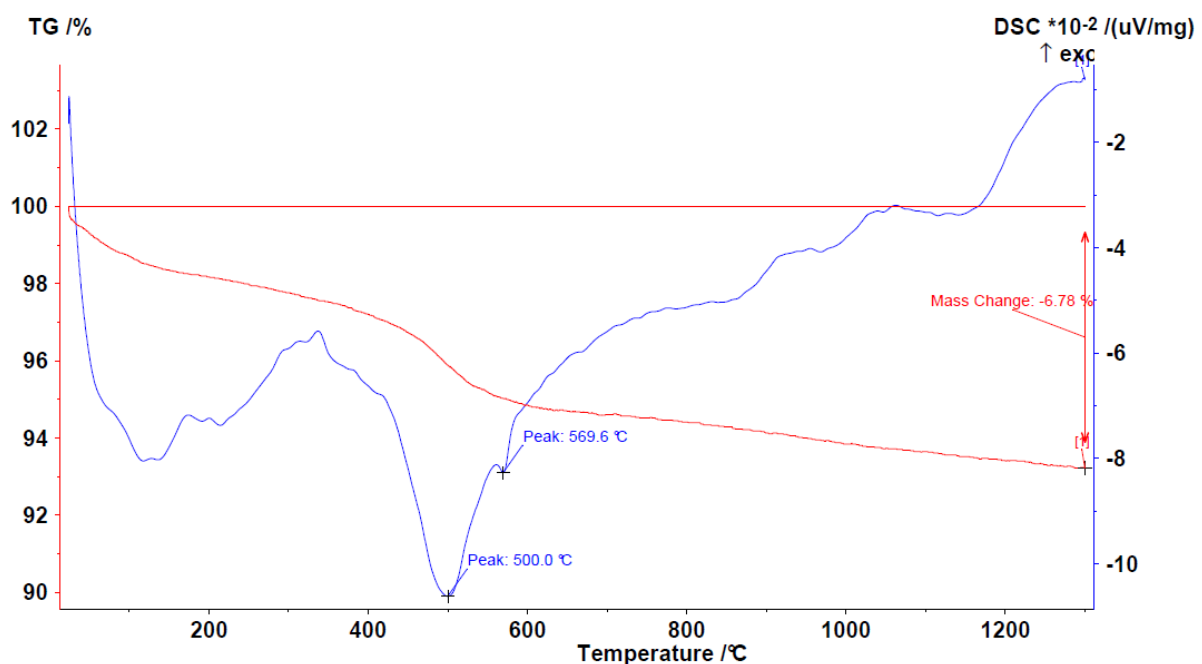


Figure 2.8. TG/DSC pumice-based sample (P4).

Optical dilatometry was performed on the standard and on L4 and P4 samples, and the results can be seen in **Figure 2.9**, **Figure 2.10** and **Figure 2.11**, respectively. This technique allows to estimate the temperatures corresponding to the beginning of sintering and the maximum sintering rate. There are two curves in each Figure: a blue curve that represents the sintering curve and describes the behavior of the sample (expansion/shrinkage) as temperature increases and a dark pink curve that is derivative of the previous curve and allows the maximum sintering speed to be identified.

Dilatometric analysis of the reference shows that there is an initial phase of loss of body water, structural water and organic matter up to about 500°C, followed by an expansion phase at which sintering begins, and finally from about 1000°C there is the vitrification phase with shrinkage of the ceramic piece. The ideal maximum firing temperature of the mixture is 1204°C which corresponds to a shrinkage of about 3.2%.

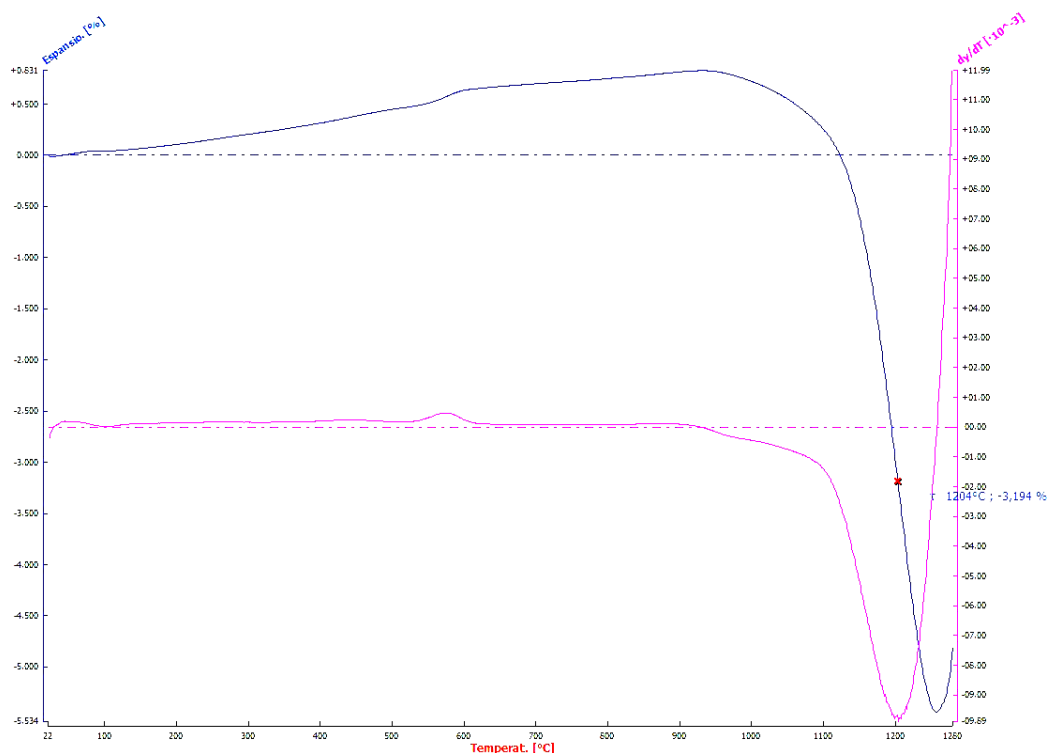


Figure 2.9. Dilatometric analysis of reference.

Dilatometric analysis of the lapillus-based sample shows that there is again an initial phase of loss of body water, structure water and organic matter up to about 500°C, followed by an expansion phase at which sintering begins, and finally from about 900°C there is the sintering

with viscous liquid phase where shrinkage of ceramic pieces occur. The ideal maximum firing temperature of the mixture is 1205°C which corresponds to a shrinkage of about 3.9% (**Figure 2.10**).

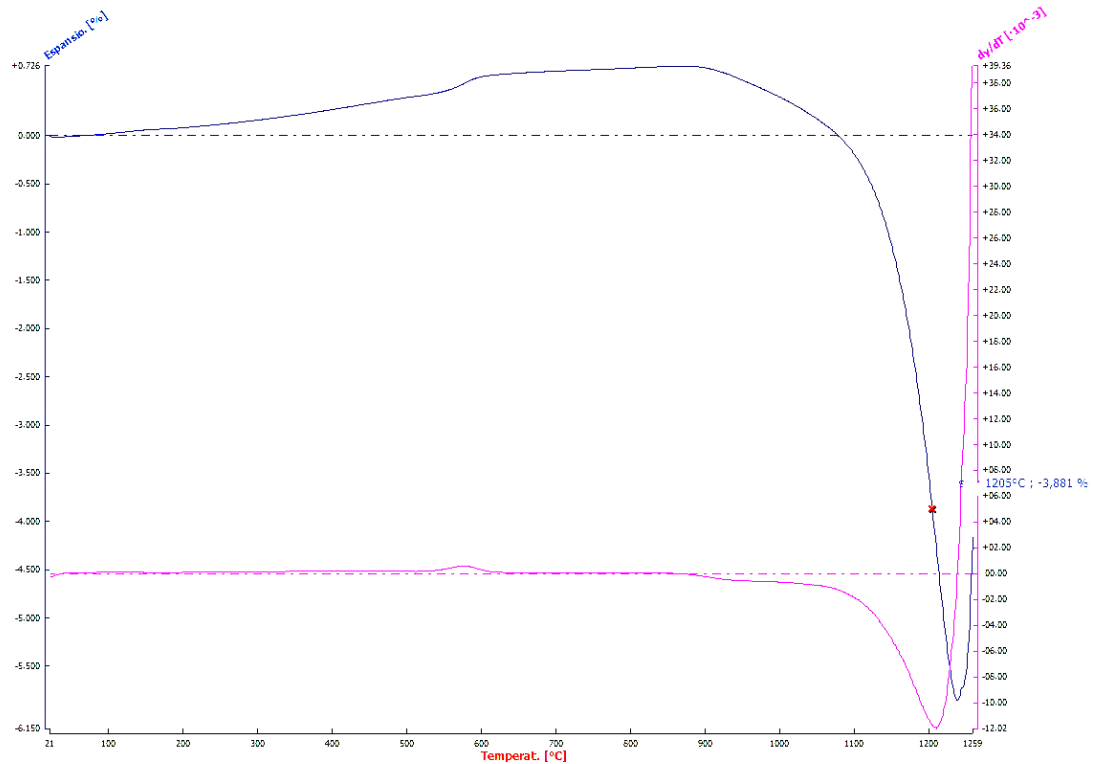


Figure 2.10. Dilatometric analysis of lapillus-based sample.

The pumice-based sample exhibited loss of body water, structure water and organic matter up to about 500°C, a subsequent expansion phase (sintering), and from about 900°C the sintering with viscous liquid phase permits the shrinkage of the ceramic piece. The ideal maximum firing temperature of the body is 1201°C to which corresponds to a shrinkage of about 4.1% (**Figure 2.11**).

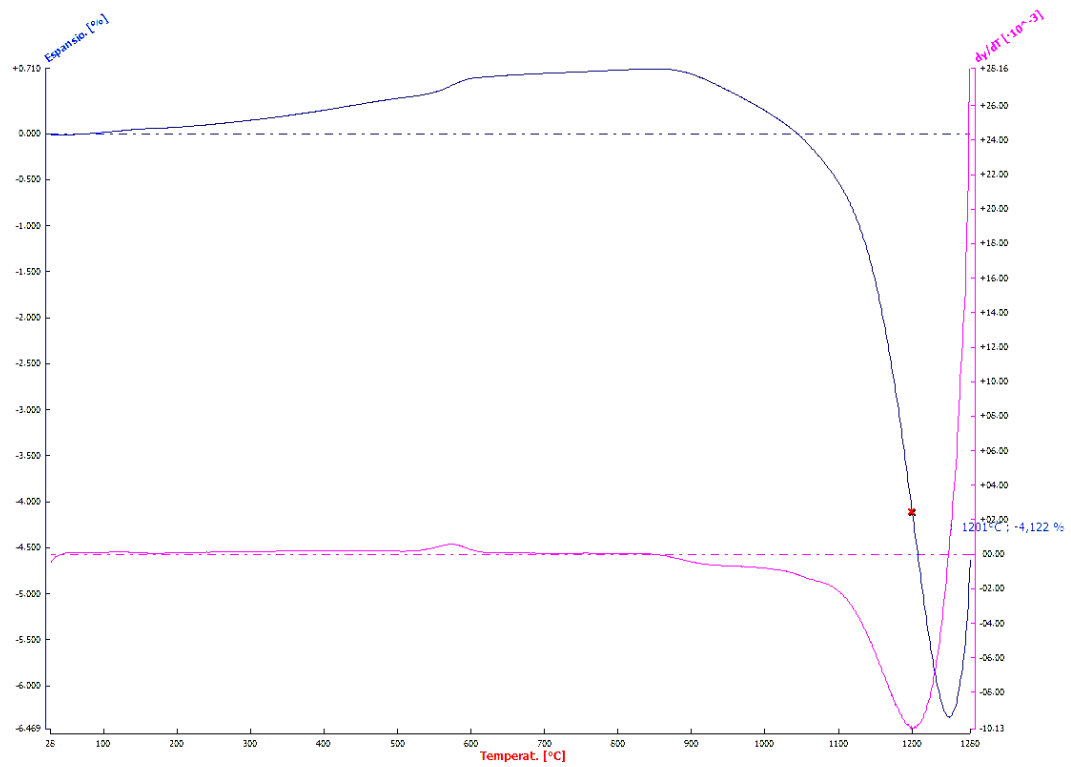


Figure 2.11. Dilatometric analysis of pumice-based sample.

The greatest shrinkage is evident in the pumice-based mixture. The ideal temperatures at the inflexion points are very similar to each other, but the pumice-containing formulation is slightly lower, probably due to the fact that as the maximum allowable temperature increases, the linear shrinkage of the ceramic piece increases.

2.5.3 CHARACTERIZATION OF FIRED SAMPLES

Linear shrinkage, water absorption and loss of ignition were evaluated on the fired samples, and the values obtained can be seen in **Figure 2.12**.

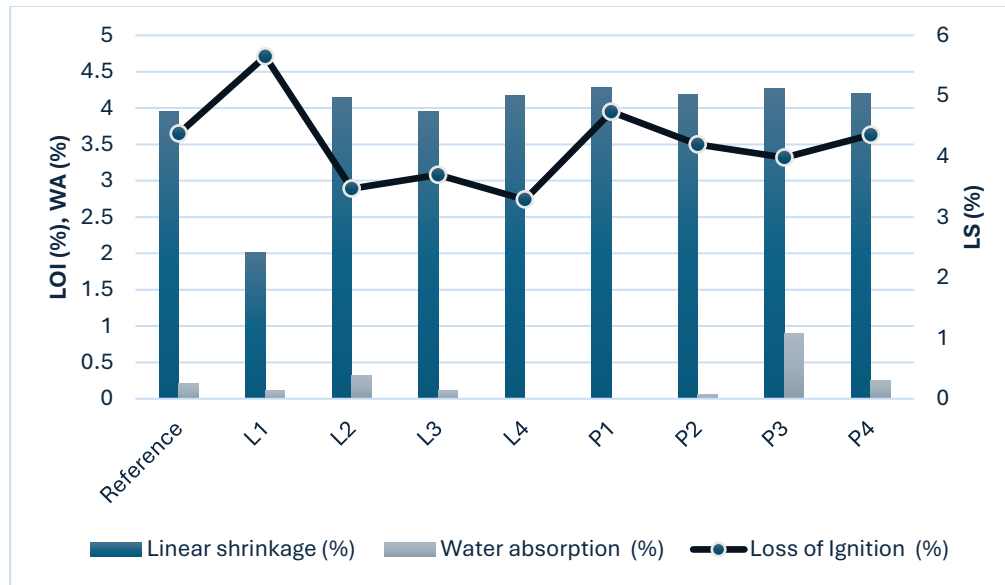


Figure 2.12. The blue line describes Loss on Ignition (LOI%), while the blue and gray columns indicate Linear Shrinkage (LS%) and Water Absorption (WA%), respectively.

The loss on ignition value obtained for the samples is similar to the standard one except for samples L1 (higher). The weight variation of the samples is monitored because it gives an indication of the amount of oxidizable substances that could potentially cause problems during the firing process.

The standard presented a linear shrinkage value ranging from 4.6-4.9%. Sample L1 presented a very low shrinkage so it can be inferred that it sintered less than the others at the same temperature. This could be attributed to the lower presence of Italian feldspar along with the presence of a mix of raw and fired ceramic scraps (chamotte) within the mixture. The other samples lapillus-based presented values that were within or very close to the range of variation of the reference. As for the samples containing pumice in all cases, linear shrinkage took higher values than the reference.

Water absorption is a normative parameter, and thanks to it, it is possible to categorize ceramic tiles according to their open porosity. International standards EN 14411 - ISO 13006 classify tiles according to the percentage of water absorption as follows:

- BIa: WA (%) $\leq$ 0.5%;

- BIb-BIIa: $3\% < \text{WA} (\%) \leq 6\%$;
- BIIb: $6\% < \text{WA} (\%) \leq 10\%$;
- BIII: $\text{WA} (\%) > 10\%$

B indicates that the product was formed by pressing.

The reference is a porcelain stoneware tile that falls into class BIa (water absorption $< 0.5\%$). Based on the reported values, tiles can be obtained from all mixtures that fall in the same class as the standard except for the P3 mixture, which has a higher value. The water absorption was evaluated on unglazed samples, so it can be deduced that the value could be further reduced, as the glaze could close the open porosity of the sample. It can be seen that samples L2 and L3 have a variation in the value of absorption, and this could be due to the inclusion of Italian sands in L3 leading to the decrease in the value of this parameter. Most of the samples, although unglazed, showed acceptable water absorption values, and this could be explained by the increased content of alkaline-earth oxides in the formulations studied (**Figure 2.12**), in agreement with literature data [160][161].

Mechanical dilatometry was performed on the reference, L4 and P4 samples but also on the glaze and engobe used in the company to assess the dilatometric agreement of the mixtures studied with the latter. The data of thermal expansion coefficient obtained by this technique are shown in **Table 2.6**.

Table 2.6. Linear Thermal Expansion Coefficient (α).

α	α (100-400°C)	α (200-400°C)	α (200-500°C)	α (100-500°C)
Reference	8.52E-06	8.79E-06	9.09E-06	8.81E-06
Glaze	7.48E-06	7.64E-06	7.64E-06	7.52E-06
Engobe	8.03E-06	8.30E-06	8.64E-06	8.36E-06
L4	8.24E-06	8.52E-06	8.88E-06	8.58E-06
P4	8.49E-06	8.75E-06	9.09E-06	8.81E-06

When glaze and mixtures containing clay are heated, they expand. As they cool, they shrink. The best situation is when the support shrinks a little more than the glaze; this keeps the glaze in slight compression. If the glaze shrinks more than the support, there is cracking creating small fracture lines (“cavillo” defect). If the glaze shrinks less than the support it is subjected to compression, which being too high causes it to peel off, especially at the edges, or the glaze clumps leaving the surfaces of the support exposed [162].

The coefficients obtained show that there is a dilatometric agreement between glaze, engobe and samples L4 and P4.

Sample P4 shows values very close to those of reference, while sample L4 shows T.E.C. values lower than the standard. Thus, it can be assumed that the studied compositions could be substituted for the reference without making ad hoc glazes or engobes for the new substrates in question.

Colorimetry was performed with the CIE L*a*b system, most widely used in the ceramic industry. This method allows the color of tiles to be determined by measuring the three parameters L* (brightness) from absolute white L=100 to absolute black L=0, a* (red-green), b* (yellow-blue) processed from the visible spectra. **Table 2.7** shows the results obtained.

Table 2.7. CIELab values obtained for the best samples compared to the reference.*

	L*	a*	b*	ΔE*
Reference	59.69	4.48	10.91	0
L4	48.73	1.34	5.42	12.66
P4	52.98	2.36	10.29	7.06

A decrease in L*, a*, b* parameters was seen with the presence of pumice and lapillus in the composition. Comparison between the reference and the pumice-based sample showed that the latter was greener and darker. On the other hand, comparison between the reference sample and the lapillus-based sample shows that the presence of lapillus makes the color darker and closer to the blue zone.

2.6 PART 2 - REPLACEMENT OF GERMAN CLAY WITH ITALIAN ONE IN PORCELAIN STONEWARE MIXTURE: RESULTS AND DISCUSSION

2.6.1 CHARACTERIZATION OF CLAYS

German ball clay and Italian red clay were characterized chemically, mineralogically and thermally to assess the similarities and differences between them.

Chemical and mineralogical analysis can be seen in **Table 2.8**.

Table 2.8. Chemical, elemental and quantitative mineralogical analyses of clays (Font: Ceramic suppliers).

Chemical analysis			
Oxide (wt%)	German ball clay	Italian red clay	
SiO ₂		65.50	67.10
Al ₂ O ₃		21.20	19.80
Fe ₂ O ₃		1.86	2.50
TiO ₂		1.27	0.80
CaO		0.32	0.72
MgO		0.54	0.74
K ₂ O		2.22	2.50
Na ₂ O		0.22	1.80
L.O.I.		6.66	5.00
Elemental analysis			
(%)	German ball clay	Italian red clay	
C		0.17	0.18
S		0.10	0.05

Mineralogical analysis			
(%)	German ball clay		Italian red clay
Quartz		39	40
Kaolinite		33	34
Illite/Mica		23	14
Plagioclase/Orthoclase		-	8
Other		5	-

Chemical analysis, performed by X-ray fluorescence spectroscopy and provided by the raw material producers, allow to say that the two clays are comparable to each other in terms of SiO_2 and Al_2O_3 contents. The kaolinitic clay has a higher Fe_2O_3 content than the ball clay but a lower TiO_2 content therefore the sum of the chromophores seems to be comparable in the two cases. The presence of higher Fe_2O_3 content could change the densification process as observed by other authors [103][104][111]. The Italian kaolinitic clay contain a high Na_2O content, and a slightly higher K_2O content. The alkali oxides increase the fusibility of the system [160] and thus could prolong the liquid phase and risk obtaining a less sintered product. The sum of alkali-earth oxides, CaO and MgO , is 0.86% for German ball clay and 1.46% for Italian kaolinitic clay. On the other hand, ball clay shows a higher loss by combustion than the kaolinitic clay, probably this could be due to the presence of organic carbon and sulfur.

The quantitative mineralogical analysis showed that the two clays are equal in quartz and kaolinite content. Ball clay contains more illite while kaolinitic clay contains illite and feldspar. Higher illite content results in more plasticity so Italian kaolinitic clay will be less plastic. The potassium in the German ball clay most likely can be linked to the presence of illite while the sodium, calcium and potassium detected in the Italian kaolinitic clay could be linked to the presence of plagioclase and orthoclase.

The thermal analysis performed on German ball clay is shown in **Figure 2.13** while on Italian kaolinitic clay in **Figure 2.14**. The red curve (TG) shows weight loss while the blue curve (DTA) describes the endo-exo events:

- Total weight loss is slightly lower in the case of kaolinitic clay (~ 7.4% vs. ~ 8%) confirming the LOI results;
- The endo event loss of zeolitic water occurs up to higher temperatures for ball clay, but is quantified as a weight loss of about 3% in both cases;
- At temperatures between 487°C and 570°C, the endo events are associated to the dehydroxylation, most likely the second peak, which occurs at the same temperature in the two clays, is given by the transformation of kaolinite to metakaolinite with loss of the water of crystallization, resulting in a large weight loss;
- Around 980 °C for ball clay and around 975°C for kaolinitic clay, there is an exothermic peak probably related to the formation of mullite without weight variation.

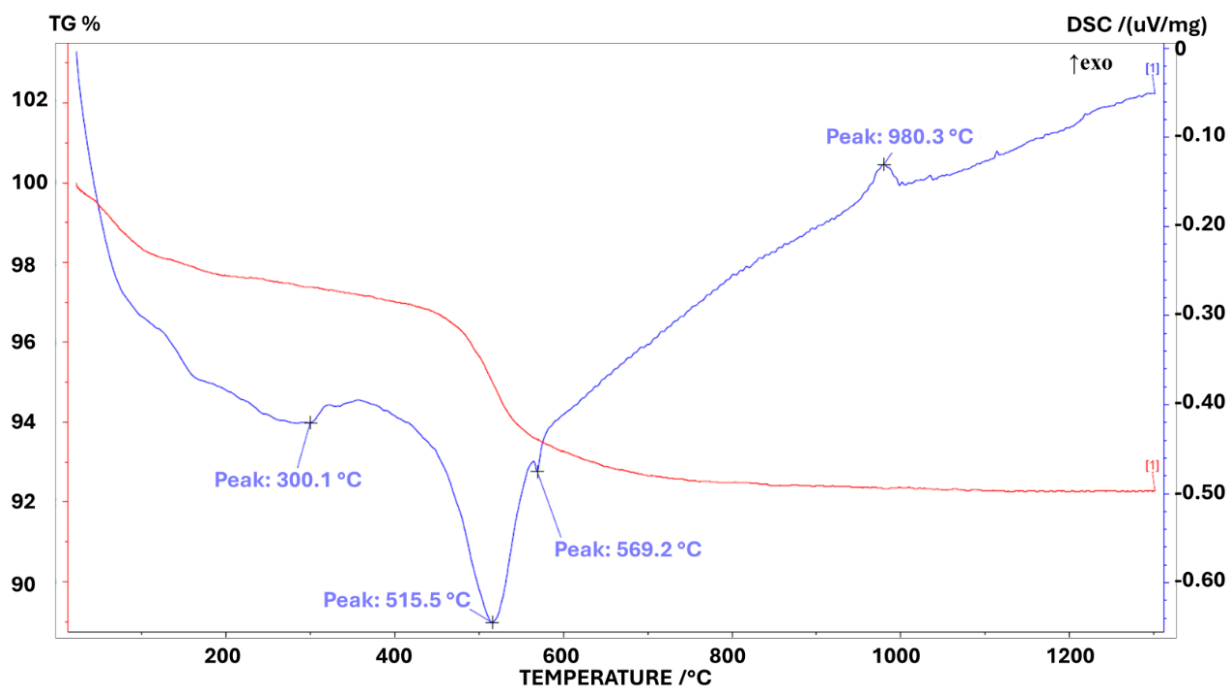


Figure 2.13. Thermal analysis of German ball clay.

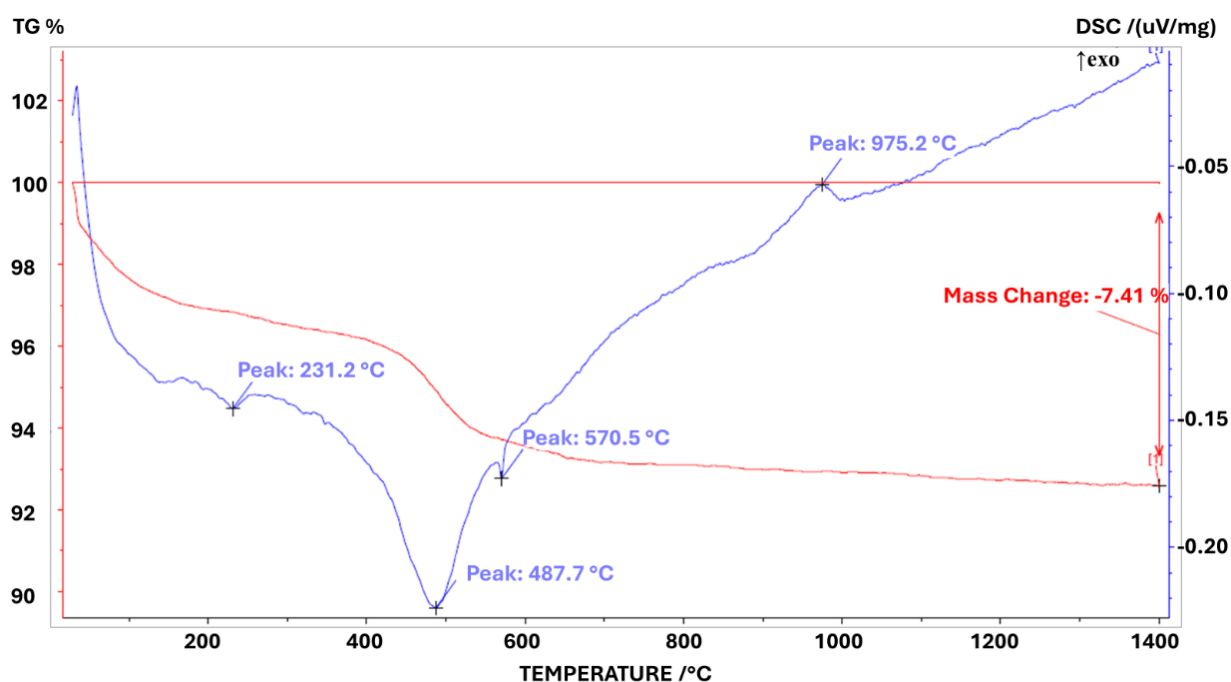


Figure 2.14. Thermal analysis of Italian kaolinitic clay.

2.6.2 SLIP AND GREEN SAMPLES CHARACTERIZATION

Table 2.9 shows the variation of the analyzed parameters on the slip and unfired samples.

Table 2.9. Analyzed parameters on slip and unfired samples.

	L0	L25	L50	L100	P0	P25	P50	P100
Efflux time (s)	16±0.5	18±0.5	22±0.5	n.a.	21±0.5	22±0.5	37±0.5	n.a.
Density (kg/m³)	1.731±0.0	1.727±0.0	1.725±0.0	1.773±0.0	1.723±0.0	1.714±0.0	1.717±0.0	1.732±0.0
Residual fraction (g)	3.65±0.01	3.91±0.01	4.14±0.01	4.88±0.01	3.48±0.01	3.59±0.01	3.68±0.01	4.14±0.01
Green flexural strength (MPa)	40.28±0.5	42.21±0.5	39.64±0.5	37.83±0.5	41.3±0.5	34.03±0.5	28.07±0.5	26.05±0.5
	0	0	0	0		0	0	0

Considering the efflux time, it can be said that this parameter tends to increase as the Italian kaolinitic clay content increases. In the case of the lapillus-based mix it is possible to note that, except in the sample containing 100% Italian kaolinitic clay, the values obtained are still acceptable as an industrial parameter. Probably a problem occurred during the measurement of the efflux time of sample L100, a problem occurred, such as a few grains clogging the outlet hole, and did not allow its proper evaluation. In the case of the pumice-based mixture, on the other hand, already with the substitution of 50% clay, the efflux time turns out to be high; therefore, as a result, the efflux time for sample P100 could not be evaluated. The limit value of efflux time, which can be considered acceptable on the laboratory scale, is 50 seconds.

The value of density is related to the efflux time one, normally as efflux time increases, density also increases. As can be seen in both cases, the formulations containing 100% substitution, and which exhibited unmeasurable efflux time values showed higher density values. In general, density tends to maintain similar values up to 50% replacement rates in both the lapillus-based and pumice-based mixtures. To decrease density values and obtain measurable viscosity values, it will be necessary to add more water during grinding.

The residual fraction represents an important process parameter, and from the values given in the table it is possible to say that this increases as the content of Italian kaolinitic clay inserted increases. In all cases the grinding time of the mixtures was 7 minutes. Most likely as the content of Italian kaolinitic clay within the mix increases, it will be necessary to extend the grinding time by a few minutes (at laboratory scale).

During the production process, the tiles must be able to resist the stresses to which they may be subjected during transport within the plant to move from one production stage to another; for this reason, the flexural strength on the unfired product was calculated. In the case of the lapillus-based mix, the flexural strength tends to decrease as the percentage of clay replacement increases but remains at fairly high values. In the case of the pumice-based mixture, the values decrease markedly when more than 25% clay is replaced. The green bending strength is positively correlated with the kaolinite content and negatively related to the coarser particle fraction as reported by *Dondi et al.* [163]. It must be considered that these are still process parameters that can be improved by modifying the recipe and perhaps substituting some raw materials.

2.6.3 CHARACTERIZATION OF FIRED SAMPLES

The samples were characterized by evaluating their physical, mineralogical, microstructural and aesthetic properties.

The physical properties analyzed were loss on ignition, water absorption and linear shrinkage whose values are reported in **Table 2.10**.

Table 2.10. Loss on ignition (LOI %), water absorption (WA %) and linear shrinkage (LS %) of fired samples.

	L	L25	L50	L100	P	P25	P50	P100
LOI (%)	3.29±0.10	3.35±0.10	3.24±0.10	2.94±0.10	3.70±0.10	3.50 ±0.10	3.11±0.10	3.31±0.10
WA (%)	0.05±0.01	0.10±0.01	0.06±0.01	0.19±0.01	0.12±0.01	0.22±0.01	0.35±0.01	0.47±0.01
LS (%)	4.46±0.05	4.46±0.05	4.94±0.05	6.12±0.05	4.94±0.05	5.36±0.05	5.56±0.05	5.66±0.05

Loss on ignition (LOI) values are comparable with each other. The mixture containing a higher percentage of Italian kaolinitic clay has lower loss on ignition, this may be due to a lower presence of oxidizable substances in Italian kaolinitic clay than the German ball clay.

The Italian kaolinitic clay has a coarser grain size than the German ball clay and, this can be inferred from the residual fraction values (*section 2.5.2*). The presence of harder minerals such as quartz and kaolinite led to a larger grain size, which may have changed the firing behavior of the samples. Italian kaolinitic clay is less plastic, and the increase in porosity could be due to this, as porosity may have been created on the green during pressing. Clays with higher illite content are more plastic and tend to fill the pores better during pressing. A less plastic clay with a larger grain size might have led to a different result than would be expected: usually, as the average grain size increases, water absorption increases, and linear shrinkage decreases [102][103][104]. However, these unconventional porcelain stoneware bodies, as shown in previous work by the authors, tend to have the opposite behavior: if shrinkage increases, absorption increases in turn [148]. A higher presence of quartz and kaolinite (2%) in Italian kaolinitic clay compared to German ball clays made the mixture more refractory. The presence of feldspars in kaolinitic clay contributes to sintering and thus to increasing linear shrinkage during firing. Again, iron increases the liquid phase around temperatures of 1130°C [104] helping the densification phase and increasing linear shrinkage. However, the presence of iron

also goes to affect water absorption values because, during firing, as it reduces, it contributes to gas formation by creating porosity and increasing water absorption.

It should be kept in mind that compositionally there are not great differences between the two clays, however, in this case, the variables to be considered increase because of the starting mix, which is not a conventional porcelain stoneware mix since it contains rocks such as pumice or lapillus that affect the behavior of the starting material.

In general, it is possible to say that the water absorption values are very different between pumice-based and lapillus-based mixtures. In each case, as the Italian kaolinitic clay content increases, this value tends to increase, but all values are less than 0.5 % (BIa group).

The linear shrinkage values are higher in samples L100 and P100 than in L0 and P0. It is possible to hypothesize that the higher presence of fluxing components (Fe_2O_3 , MgO , CaO , Na_2O , K_2O) in the Italian clay (8,26%) with respect to German clay contributes to the sintering and densification process.

Mineralogical analysis was performed on all fired samples (**Figure 2.15**, **Figure 2.16**). In **Figure 2.15** and **Figure 2.16**, the lower curves represent the spectrum of sample L0 and P0 respectively, which contain German ball clay, while the upper curves are for samples L100 and P100 respectively, thus containing only Italian kaolinitic clay. In both figures, an elevated curve can be seen on the right side between the 5° - 33° 2 Theta positions of the spectra, indicating the presence of a glassy phase, normally present in this type of body.

Porcelain stoneware undergoes complex transformations during firing in terms of the mineral constituents of the mixture. The resulting products contain a vitreous phase usually associated with quartz, mullite, and feldspars. Quartz (SiO_2) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) were detected in both batches of products. Clay minerals around 1000 °C form mullite due to the reaction between Al_2O_3 and SiO_2 , contained in the raw materials, especially kaolinitic ones [103]. The formation of mullite is responsible for the enhanced mechanical properties of porcelain stoneware.

The lapillus-based batch also showed the presence of feldspars, orthoclase ($\text{K Al Si}_3 \text{O}_8$) and albite ($\text{Na (Al Si}_3 \text{O}_8)$). As the content of Italian kaolinitic clay increases, the content of SiO_2 and K increase in the mixture, and the intensity of quartz peaks tends to increase as well as that of orthoclase.

In the pumice-based batch, unlike the lapillus-based batches, both mullite and quartz peaks tend to decrease this despite the fact that the amount of iron in the mixture is lower [103]; this could

be due to a higher presence of potassium contributed not only by Italian kaolinitic clay but also by pumice [143].

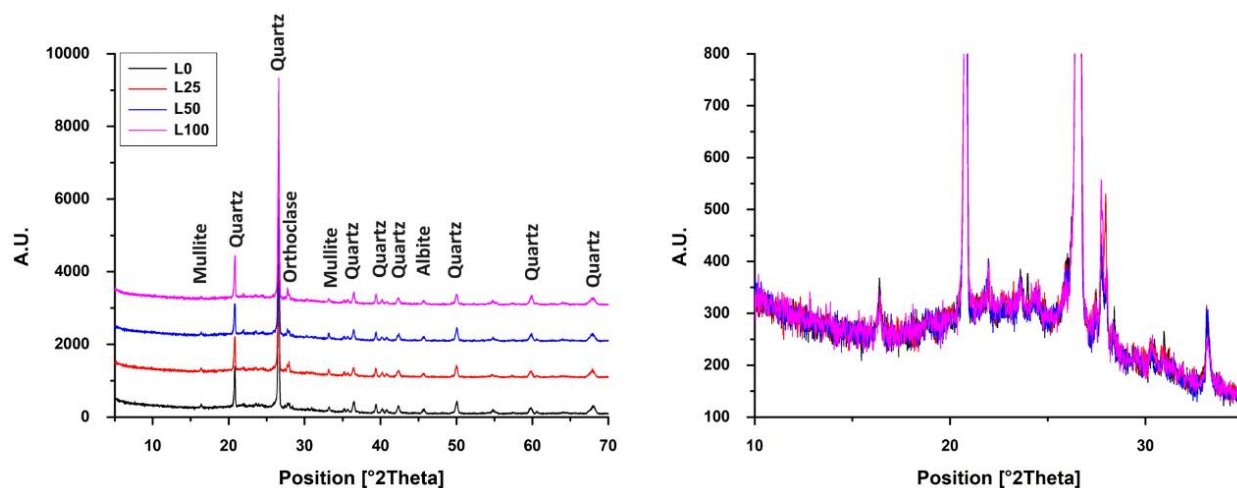


Figure 2.15. Mineralogical analysis on lapillus-based materials. On the left there are the spectra of the formulations, with the percentage of Italian kaolinitic clay increasing from bottom (L0) to top (L100). On the right, magnification between 10° and 30° 2 theta to highlight the presence amorphous phase.

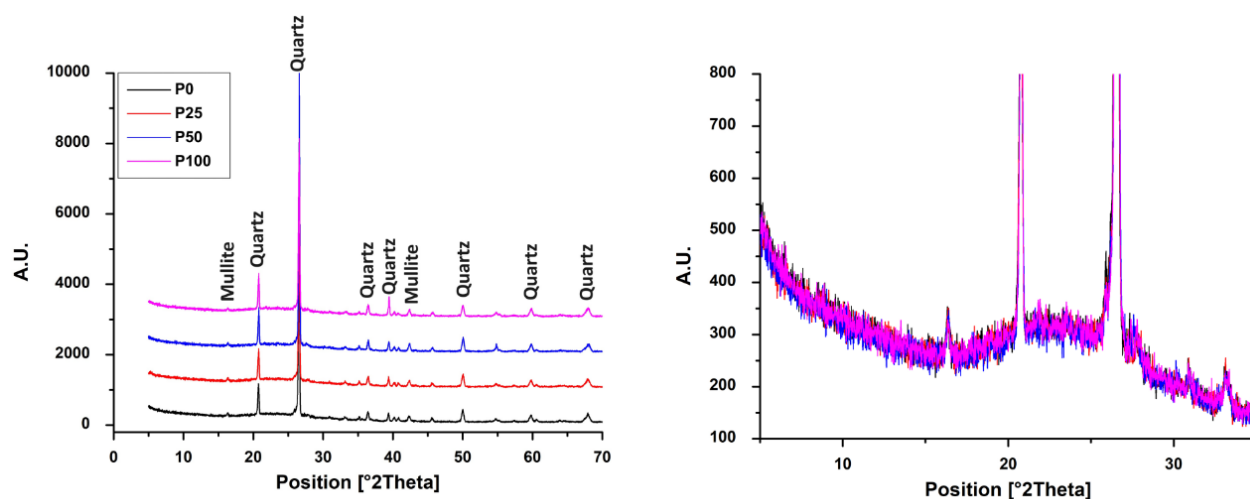


Figure 2.16. Mineralogical analysis on pumice-based materials. On the left there are the spectra of the formulations, with the percentage of Italian kaolinitic clay increasing from bottom (P0) to top (P100). On the right, magnification between 10° and 30° 2 theta to highlight the presence amorphous phase.

Regarding microstructural analysis, ESEM images of the lapillus-based samples can be observed in **Figure 2.17 (a-d)**. The images were acquired in secondary electron mode. Images (a) referring to sample L0 show diffuse porosity, with pores of various sizes. There are many small pores ($<10\text{ }\mu\text{m}$) and some larger ones that reach sizes on the order of $45\text{-}50\text{ }\mu\text{m}$. Looking at the L25 (b), L50 (c) and L100 (d) samples, it is possible to see that as the Italian kaolinitic clay content increases, the porosities are still widespread, but the small pores decrease, and the larger pores increase. It also appears that the shape of the pores is more regular in the sample containing only German ball clay and that as the percentage of clay replacement increases pores show increasingly irregular shapes. The presence of the diffuse porosity and the increase in pore size also confirm the results obtained from the water absorption; this adsorption increases, making the material less resistant to stress due to the voids that are formed.

Another observation that can be made relates to the presence of the amorphous phase, which seems to increase as the amount of German ball clay decreases, and these results appear to agree with the diffractometric analysis performed on the samples, where the presence of glassy phase was revealed.

Sample L0 compared to the other samples appears to be more sintered while L100 is the one that would appear to be less densified.

ESEM images of the pumice-based samples can be observed in **Figure 2.17 (a-d)**. The P0 sample, identified by (e), shows a spherical porosity with a size of $10\text{ }\mu\text{m}$ and an intergranular porosity with a size of $30\text{ }\mu\text{m}$; the pores are larger than in the lapillus-based sample containing only German ball clay. Also, in the pumice-based samples, as happened in the lapillus-based samples, the porosity increases in both size and quantity, as the Italian kaolinitic clay content increases. Samples P25 (f), P50 (g) and P100 (h) have much larger pores than their lapillus-based analogs, and this could strongly affect the flexural strength values on the fired pieces.

The pumice-based samples appear less sintered than their P0 reference but also appear less sintered than the lapillus-containing samples. The amorphous phase present could also be attributable to a lower degree of sintering or an overfiring of the samples at the industrial temperatures due to the high amount of amorphous fraction.

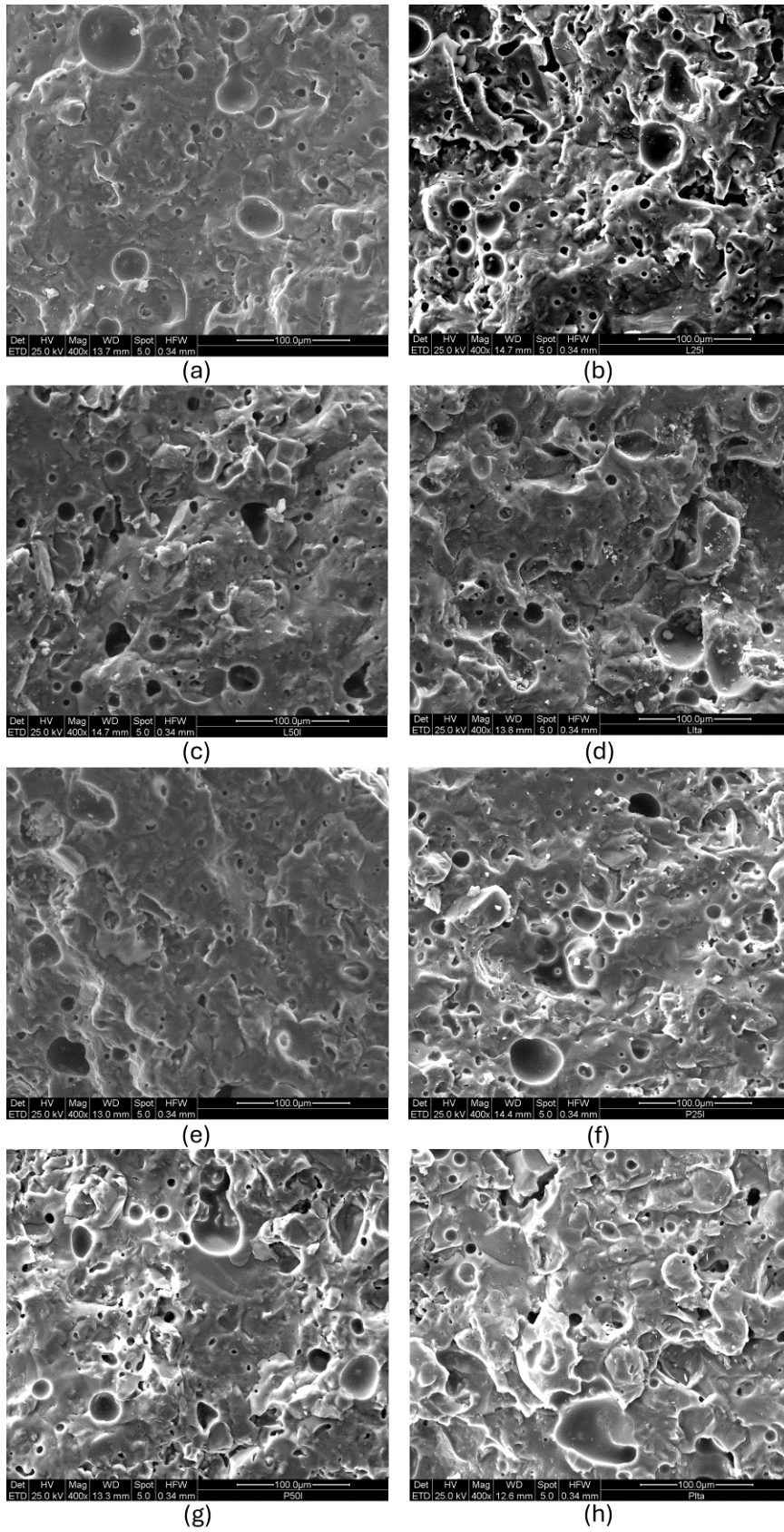


Figure 2.17. ESEM images of lapillus-based and pumice-based samples. (a) L0, (b) L25, (c) L50, (d) L100, (e) P0, (f) P25, (g) P50, (h) P100.

The aesthetic properties were evaluated by the *CIE Lab** system, which is widely used in the ceramic industry to obtain colorimetric data. The values obtained are shown in **Table 2.11**.

Table 2.11. *CIELab** values obtained for the best samples compared to the reference.

	L^*	a^*	b^*	ΔE^*
L0	46.54±0.60	1.76±0.03	5.45±0.07	-
L25	43.90±0.20	1.83±0.07	5.51±0.10	2.65±0.40
L50	43.27±0.20	2.10±0.03	5.53±0.04	3.29±0.40
L100	38.87±0.35	3.33±0.03	5.50±0.07	7.83±0.25
P0	51.07±0.40	3.55±0.05	9.74±0.15	-
P25	49.58±0.36	4.26±0.05	9.53±0.09	1.66±0.04
P50	46.22±0.80	5.83±0.10	10.20±0.14	5.38±0.34
P100	42.51±0.33	6.10±0.15	8.99±0.25	8.96±0.09

The reported values of ΔE^* (calculated by Equation 6) were obtained from the comparison with the L0 and P0 samples depending on the mixtures considered.

Looking at the values obtained for both the lapillus and the pumice samples, it can be seen that the brightness decreases with the increase of Italian kaolinitic clay in the mixture, while a^* and b^* , on the contrary, increase. Only in the case of P100, ΔE^* is lower than in the case of P50. In the case of the pumice-based mixtures, the initial value of L^* is higher due to a minor amount of iron in the composition. Regarding the ΔE^* value is also strongly influenced by the fact that the brightness tends to decrease with greater variation from one sample to another. The variation in the values shown in the table can be related to a high presence of Fe in the Italian kaolinitic clay. The colorimetric difference obtained highlights the achievement of a darker support than the previous one. This difference is positive in this case as the support tends to have a color very close to some brown glazes currently produced in the ceramic company.

2.7 PART 3 - LIFE CYCLE ANALYSIS: RESULTS AND DISCUSSION

The life cycle analysis was performed on the reference sample and the P4 and L4 samples (*Part 1*), hereafter referred to as pumice-based and lapillus-based, respectively, as previously reported.

Figure 2.18 shows the impacts associated with total tile production (m^2) compared to the year 2022. For each impact category and scenario, the comparison of total inputs and raw material transportation inputs can be seen.

It is evident that over 95% of the impacts are from the transportation of raw materials from quarries to the manufacturing site; this is even more evident in **Table 2.12**. As mentioned in *section 2.4.3*, impacts related to raw material extraction, transportation and manufacturing were considered for each scenario. **Table 2.12** shows the percentage influence of each analyzed phase on the related impacts.

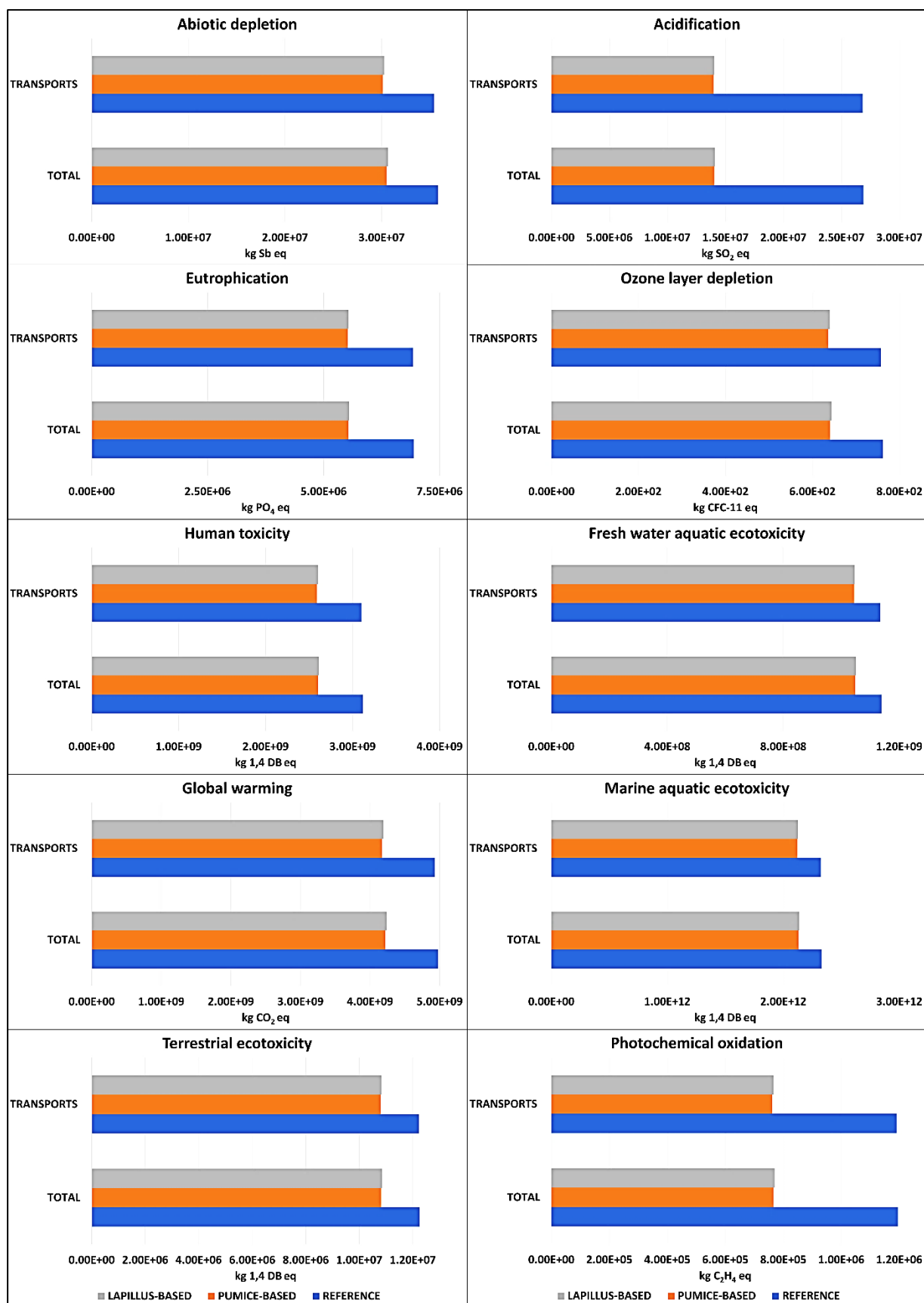


Figure 2.18. Impact categories for the three scenarios.

Table 2.12. Impact (%) corresponding to raw materials (RM), transportation (T), and manufacturing (M).

	Reference (%)			Pumice-based (%)			Lapillus-based (%)		
	RM	T	M	RM	T	M	RM	T	M
Abiotic depletion	0.07	98.93	1.00	0.05	98.78	1.17	0.05	98.78	1.17
Acidification	0.08	99.76	0.16	0.09	99.60	0.31	0.09	99.60	0.31
Eutrophication	0.10	99.80	0.09	0.09	99.79	0.12	0.09	99.79	0.12
Global warming	0.07	99.06	0.87	0.05	98.93	1.02	0.05	98.93	1.02
Ozone layer depletion	0.08	99.46	0.46	0.07	99.38	0.54	0.07	99.39	0.54
Human toxicity	0.17	99.52	0.31	0.17	99.46	0.37	0.17	99.46	0.37
Fresh water aquatic ecotoxicity	0.18	99.66	0.16	0.18	99.65	0.18	0.18	99.65	0.18
Marine aquatic ecotoxicity	0.21	99.56	0.24	0.20	99.54	0.26	0.20	99.54	0.26
Terrestrial ecotoxicity	0.11	99.80	0.09	0.10	99.80	0.10	0.10	99.80	0.10
Photochemical oxidation	0.07	99.61	0.32	0.07	99.43	0.50	0.07	99.43	0.50

Ibáñez-Forés et al. [156], in a 2013 paper on tile production in Spain, observed that recovering heat from the production cycle can achieve environmental improvements of more than 90%. In this case study, combined heat and power (CHP) significantly reduced the impact of manufacturing, as shown in **Table 2.12**. Ceramic companies are energy-intensive companies; in fact, if combined heat and power were not considered, most likely the production phase would be the most impactful in agreement with other studies [115][156].

In all cases, the pumice and lapillus scenarios show a decrease from reference. The categories that show a greater decrease in impacts are "Acidification" and "Photochemical oxidation" while those that are close to the values of the reference scenario are "Freshwater aquatic ecotoxicity" and "Marine aquatic ecotoxicity". Although the relative improvement is less evident, the absolute decrease in "Marine aquatic ecotoxicity" and "Freshwater aquatic ecotoxicity" is still relevant, as they are in the order of E12 kg 1,4 DB eq and E9 kg 1,4 DB eq respectively.

In all scenarios, the greatest impacts occur in the categories "Marine aquatic ecotoxicity", "Human toxicity", "Fresh water aquatic ecotoxicity," and "Global warming."

From a comparison between the pumice-based and lapillus-based scenarios, it is possible to say that the differences are very small. Nonetheless, pumice-based products have slightly lower impacts in most indicators. Probably the difference between the pumice-based and lapillus-based scenarios is due to the variation in the percentages of raw materials required to obtain the ceramic piece.

The impact of transportation is very high. According to literature data [114][115][117] transportation is very impactful and therefore these data could be confirmed, although normally the greatest impacts are related to production. In the case study, however, the model did not consider the real quantity of energy needed to produce the amount of porcelain stoneware manufactured by the company in 2022. This is due to the presence of a cogeneration plant capable of producing almost all the needed energy, so the company is self-powered. On the other hand, there are raw materials that travel over 8000 km to get to their destination.

Figure 2.19 shows only the data on raw material impacts. This is to better highlight the difference between the three scenarios. In the previous figures, there is no contribution related to raw materials or production because they are negligible compared to transportation, as is evidence in **Table 2.12**.

The categories "Freshwater aquatic ecotoxicity" and "Photochemical oxidation" do not show a clear change from the life cycle of the reference sample. The trend in data for raw materials alone is comparable to the total data (raw materials, transport and production): there is a decrease in all categories in the case of pumice-based and lapillus-based products. Comparison of the pumice-based and lapillus-based scenarios shows that the latter scenario showed indicators with slightly lower impacts except for the case of "Fresh water aquatic ecotoxicity".

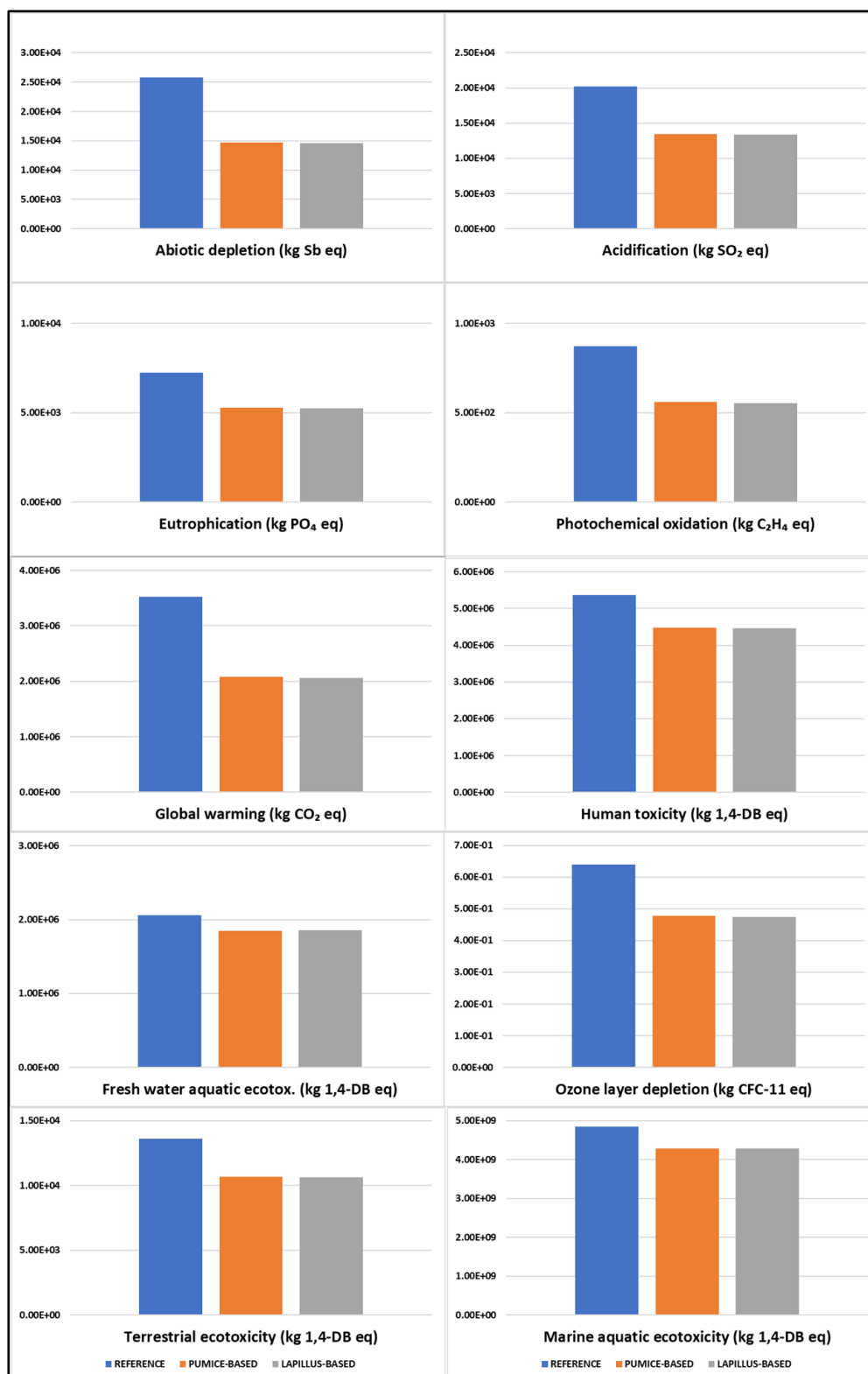


Figure 2.19. Raw materials impacts.

There has been a conscious focus on transportation and raw materials, as these are the life cycle stages that vary from one product to another. One point should be made: the number of raw

materials in the pumice-based and lapillus-based scenarios is significantly reduced when compared with the reference. Consequently, impacts are reduced. However, they remain very high because many of the raw materials in the reference scenario travel by rail and sea, while Italian raw materials travel by road. Hence, most of the transportation means used in the reference case are less impactful than those used in the other two cases.

If we shift our attention to energy consumption, it is possible to see that it is very low. Normally most of the impacts are due to the production process, as shown by other authors [153]. In the case under study, the company works in cogeneration, recovering heat and producing electricity, avoiding buying electricity from fossil sources. Energy consumption generates somewhat higher impacts than those generated by raw materials but manages to be limited.

Figure 2.20 shows the avoided impacts in the two alternative scenarios compared to the reference. The data refer to the tons of impacts avoided in the corresponding categories.

The two scenarios are very similar to each other. As mentioned earlier, pumice waste-based tile production has slightly lower impacts in most categories, and this results in a higher percentage of avoided impacts. There are environmental benefits in each category. The categories that had less environmental benefits were "Fresh water aquatic ecotoxicity" and "Marine aquatic ecotoxicity". The greatest environmental benefits, with a net decrease in impacts, were in the categories "Acidification" and "Photochemical oxidation." The other categories showed improvements between about 11% and 20%. The environmental benefits obtained are in the range of about 20% in both scenarios.

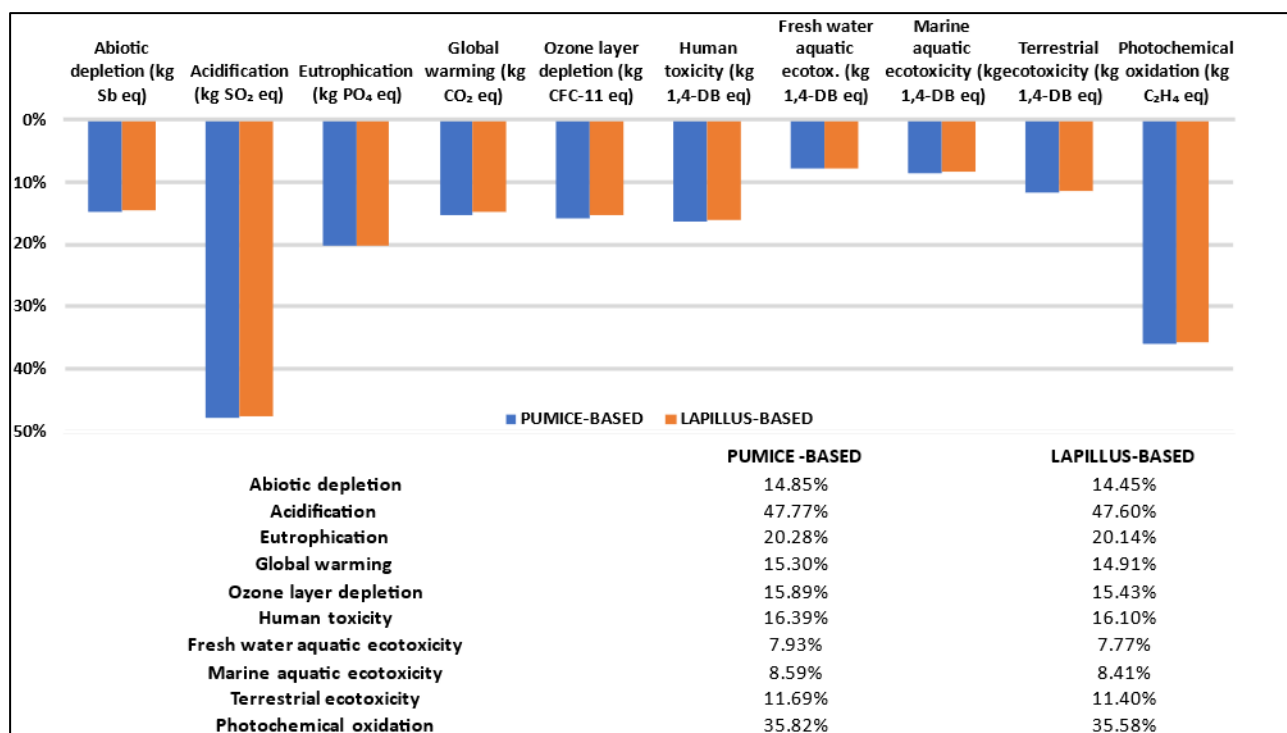


Figure 2.20. Avoided impacts.

2.8 CONCLUSIONS

In this chapter, the use of volcanic raw materials for the production of porcelain stoneware has been discussed and the environmental impact associated with their use in ceramic body has been evaluated.

In the first part ceramic bodies have been formulated by replacing foreign feldspars with about 40-50% waste and by product, of which 10-16% is constituted by volcanic scraps. Pumice and lapillus have been successfully incorporated and used not only as fluxes but also as natural colorants. The mixtures studied have shown interesting mechanical properties, low absorption, acceptable linear shrinkage and adequate dilatometric concordance with glazes and engobes currently in use, without changing the current industrial production cycle. Comparing the obtained mixtures to the reference, the number of raw materials has been decreased from 18 to a maximum of 10, at least 4 of which are recycled; the volumes of water required for the production of slip in the case of the lapillus-based mixture are reduced; and the use of artificial dyes is significantly lowered. The product thus obtained, therefore, is a good example of circular economy and sustainability.

In the second part, the German clay in ceramic supports, obtained in the first part, was progressively replaced by Italian clay, with the aim of obtaining a body consisting of Italian raw materials.

The lapillus-based mixtures studied showed low absorption, rather high linear shrinkage, and an internal microstructure similar to that of porcelain stoneware. In this case, the German clay could theoretically be totally replaced, resulting in a porcelain stoneware mix containing only Italian raw materials.

Pumice-based mixtures have shown, with replacement percentages of Italian kaolinitic clay exceeding 50%, a water absorption at the limit of what is required by the standard for a product to be classified as porcelain stoneware. In this case, it is possible to partially replace the German clay, up to 25%, to obtain technological properties similar to commercial porcelain stoneware.

In both batches, the internal microstructure of the samples changed. Although the obtained sample, by water absorption values, could be considered as belonging to the BIa group, ESEM analysis showed that there was an increase in closed porosity and some particles had not fully reacted. The densification process took place, as evidenced by an increase in the linear shrinkage value. However, the water absorption value did not drop to zero. Italian kaolinitic clay is less plastic and the increase in porosity could be due to this; therefore, although a total substitution in the lapillus mix is possible, it would be better not to completely replace the German ball clay in order to control the formation of pores and improve the technological properties of the finished products.

In the third part, the life cycle of three products was analyzed: a reference product (which is a porcelain stoneware tile currently on the market), a porcelain stoneware tile containing pumice scraps, and a porcelain stoneware tile containing volcanic lapillus scraps. The inventory analysis made it possible to evaluate the impacts deriving from the extraction and transportation of raw materials and from product manufacturing. Impact categories were evaluated with a focus on raw materials and their transportation, as they differentiated one scenario from another. The manufacturing process remained the same in all three scenarios.

It was observed that:

- a) In the two scenarios in which volcanic scraps were among the raw materials, the impacts decreased in any analyzed category;

- b) The reduction in impacts ranges from a minimum of about 8% in the "Fresh water aquatic ecotoxicity" and " Marine aquatic ecotoxicity" categories, to a maximum of about 48% in the "Acidification" category;
- c) For each scenario, transportation is responsible for more than 95% of the impact generated, followed by the production process and finally by the raw material extraction process, which only in one case generated impacts greater than 0.2%;
- d) The influence of transportation is still high in the two proposed case studies, because:
 - notwithstanding the raw materials come from Italy, they travel mainly by road, with a corresponding high impact;
 - the impact associated with energy consumption is low because the factory is almost energy self-consistent, so the impact produced by the transportation is emphasized.

Impacts could be further reduced by:

- evaluating more environmentally friendly means of transportation, as Italian raw materials currently travel by road. It would be better if they traveled by train;
- evaluating raw materials located close to the production site.

It is possible to state that pumice and lapillus-based tiles, in addition to having good technological performance, are more environmentally and human health friendly than the considered reference. Although the impacts can be further reduced, the obtained results strengthen the importance of using these types of scraps for the production of porcelain stoneware.

3. CEMENTITIOUS MORTAR

3.1 STATE OF THE ART

Cement is a hydraulic binder in the form of a fine powder which, when mixed with water, forms a paste that is able to harden. This hydraulic hardening is mainly due to the formation of calcium silicate hydrates, which are generated by the reaction between water and cement components [164][165]. The main active component of a cement is ‘Portland clinker’. Cement has been industrially produced since the mid-19th century, and today it remains one of the most widely used building materials due to its versatility and performance characteristics, being used in many areas of construction [166].

The production process is a complex and energy-intensive activity that contributes significantly to global CO₂ emissions. The traditional method involves calcining limestone (CaCO₃) and clays in a rotatory kiln to obtain clinker, which is then ground to produce cement. This process consists of several main steps: raw material extraction, preparation, calcination and grinding.

The largest amount of raw materials is for clinker production, among them are:

- Limestone: natural rock of sedimentary origin consisting essentially of calcium carbonate (CaCO₃). Limestone rich in CaCO₃ and free of impurities of an organic nature and clay accelerates the hydration process of the clinker itself and thus the initial development of the cement's mechanical strengths; it reduces the demand for water by increasing the workability of fresh concrete and increases the water retention of concrete by reducing water moisture and plastic shrinkage;
- Clay mineral mixture: mainly montmorillonite and illite (hydrated silicates of aluminium, magnesium, iron and other elements), combined with small percentages of quartz and limestone;
- Calcined schist: produced by firing at a temperature of approximately 800 °C, it contains dicalcium silicate and monocalcium aluminate, as well as small amounts of free calcium oxide and calcium sulphate, with significant proportions of reactive silicon oxide;
- Marl: provides in varying proportions CaO, SiO₂, Al₂O₃, Fe₂O₃, but requires further additions of limestone or clay materials to obtain the right chemical proportion for the production of cement raw flour;

- Cement marl: provides the raw flour with CaO , SiO_2 , Al_2O_3 , Fe_2O_3 in the right proportions for cement manufacture; in this case, it is not necessary to use other raw materials for cement flour production [167].

The cement industry requires other raw materials that must be ground together with the clinker to produce the different types of cement:

- Gypsum: calcium sulphate in the form of semi-hydrated, anhydrous gypsum or a mixture of these. It influences several cement properties (mechanical strength, shrinkage, heat of hydration development, durability etc.), but its main action concerns the regulation of setting. The regulating action takes place on the tricalcium aluminate which, in the absence of gypsum, would react rapidly with water causing the cement to set quickly. However, while small amounts of gypsum are essential to regulate setting, excess can cause expansion and cracking of the cement paste. For this reason, the tolerable sulphate content is strictly limited by standards [168];
- Pozzolanic materials: these are natural or industrial siliceous or silica-aluminate substances that do not harden when mixed with water but, when ground finely, in the presence of water they react at normal temperature with calcium hydroxide to form calcium silicate and calcium aluminate, which develop mechanical strength and have characteristics similar to those formed when hydraulic materials harden. Natural pozzolans are generally materials of volcanic origin, while calcined natural pozzolans are (natural) substances activated by heat treatment [169];
- Raw materials used for clinker production such as limestone.

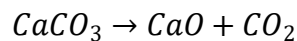
In order to be used in the production of cement, raw materials must possess specific chemical and mineralogical characteristics as requested by standard UNI EN 197-1:2011. Not all limestones, clays, pozzolans, etc., have suitable chemical characteristics for cement production; it is therefore understandable how the truly usable deposits are confined to a few, restricted mining areas despite the fact that these are relatively common rocks.

All the raw materials must be mixed to obtain a homogenous composition, after being done appropriately and, if necessary, added with correctives. These are processed into a very fine powder and sent for storage in the form of homogenized cement flour.

The cement raw flour mixture, heated by contact with hot gases, enters the rotary kiln where the transformation of the fired material takes place until the clinker, whose components give the cement its hydraulic activity, is formed at a temperature of 1450-1500 °C.

The furnace is divided into zones with increasing temperatures:

- Preheating (100°C - 800°C): evaporation of water and decomposition of clay minerals;
- Calcination (800°C - 1000°C): calcium carbonate decomposes into calcium oxide and carbon dioxide:



- Sintering (1200°C - 1450°C) → reactions occur between CaO, SiO₂, Al₂O₃ and Fe₂O₃ resulting in formation of minerals of clinker:
 - Alite (C₃S - tricalcium silicate): gives mechanical strength;
 - Belite (C₂S - dicalcium silicate): increases the durability of cement;
 - Tricalcium aluminate (C₃A): accelerates setting time;
 - Ferro aluminate tetracalcium (C₄AF): improves workability.

The CaO/SiO₂ mass ratio must not be less than 2.0 and the magnesium oxide content must not exceed 5.0% by mass [167][170].

For ease of discussion, each oxide has been replaced with a capital letter, as described in **Table 3.1**.

Table 3.1. Identification of main oxides.

SiO ₂ = S	CaO = C	MgO = M
Al ₂ O ₃ = A	K ₂ O = K	
Fe ₂ O ₃ = F	Na ₂ O = N	H ₂ O = H

At the end of the firing process, clinker is obtained, a granular material that is rapidly cooled with air jets to prevent recrystallization and maintain the desired properties.

The clinker is then ground with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which regulates the setting time, with any additional materials (blast furnace slag, pozzolan, limestone) and with any additives (fluidizers, accelerators, delayers, etc.).

The cement thus obtained is packaged in bags or distributed loose for use in construction and infrastructure.

The cements covered by EN/197-1 are divided into five main classes:

- **CEM I Portland cement:** must contain at least 95% clinker and between 0-5% minor constituents. They are generally used in the pre-casting of simple and prestressed reinforced concretes;
- **CEM II Composite Portland Cement:** consists of clinker, which can be between 65-94% and granulated blast furnace slag/silica fume/pozzolanic ash/fly ash/calced shale/limestone. They have properties very similar to those of CEM I, which make them suitable for the most common uses in the construction of normal and prestressed reinforced concrete and precast elements;
- **CEM III Blast-Furnace Cement:** these consist of up to 64% clinker and basic granulated blast furnace slag. This type is divided into three sub-types with slag contents ranging from 36% to 95%. CEM III are mainly indicated in situations where concrete is subject to chemically aggressive environments and for the construction of large-scale works;
- **CEM IV Pozzolanic cement:** these consist of clinker between 45 and 89% and natural or artificial pozzolanic material varying between 11% and 55%. They present a high resistance to chemical attack;
- **CEM V Composite cement:** they are composed of a mixture of clinker, blast furnace slag and pozzolanic material and are suitable for making concrete exposed to moderately aggressive environments such as seawater, acid water, sulphate soils, etc.

In addition to the types already described, there are special cements on the market that are formulated for specific uses (sulfate resistance, high strength, quick-setting concretes).

The composition or proportion of the constituents gives the hydrated product, in addition to its mechanical properties, specific characteristics of resistance to chemical or chemical-physical attack. The type of cement influences the ability to maintain the strength characteristics of the mixture obtained (mortar or concrete) over time [167][170][171].

Sustainability in the cement supply chain is a critical topic as cement is one of the most widely used materials in the construction industry, with global production exceeding 4 billion tons per year in 2022 [172][173]. Cement production is also a major source of carbon dioxide emissions, as reported earlier, and its production is estimated to be responsible for 5-9% of global greenhouse gas emissions [174][175]. The liming process releases large amounts of CO₂ from both the combustion of fossil fuels and the decomposition of limestone, the latter generating 60% of total emissions. The main environmental impact is related to (i) CO₂ emissions: clinker production contributes about 90% of the CO₂ emissions of the process; (ii) energy consumption: clinker calcining kilns require huge amounts of energy, mainly derived from fossil fuels; and (iii) degradation of natural resources: raw material extraction causes soil erosion and loss of biodiversity [176].

The goal of reducing the environmental impact of cement has led to intensive academic research aimed at improving the sustainability of this material. Key strategies include the search for alternative cement (LC3, geopolymers) and the partial replacement of clinker with materials with lower environmental impact, known as supplementary cementitious materials (SCMs) [177][178][179]. These materials are usually industrial by-products or natural materials that can help reduce CO₂ emissions while improving some cement properties. Among the most promising materials are:

1. *Fly ash*: A by-product of coal combustion in thermal power plants. Their chemical composition makes them an excellent substitute for clinker, as they can improve the durability and reduce the permeability of concrete. In 2023, a study explored the use of coal fly ash along with other industrial by-products, such as slag, to develop low-carbon cementitious materials. This study highlighted the material's ability to improve mechanical properties while reducing the environmental impact of traditional cement blends. The use of coal fly ash in cement production is supported by their pozzolanic properties, which allow them to react with calcium hydroxide to form additional cementitious compounds, thereby improving the durability and strength of the resulting concrete [180]. In addition, fly ash has been found to maintain mechanical integrity in 3D printed concrete, particularly in combination with other waste materials such as ground waste glass. This approach not only promotes recycling but also supports innovative construction techniques such as 3D printing, further reducing the demand for conventional concrete [181]. The problem with coal fly ash is their decrease in the next years due to the general decrease of the use of coal as fuel.

2. *Blast-furnace slag*: Derived from steel production, these slags are already widely used in blast-furnace cements. Slag can contribute to a significant reduction in emissions while improving the mechanical and durability properties of concrete. World production of blast-furnace slag was about 530 million tons about 10 years ago, of which only 65% was used by the construction industry [182]. *Siddique and Bennacer* [183] analyzed the effect on the physical and chemical properties and hydration reaction of using granulated and ground blast furnace slag within high-quality cement and concrete paste/mortar. They also evaluated the workability, setting time, compressive strength, chloride and sulfate resistance of the cement paste and mortar. *Majhi et al.* [184] used recycled coarse aggregates instead of natural ones and ground granulated blast furnace slag as a substitute for ordinary Portland cement to develop sustainable concrete. *Sharmila and Dhinakaran* [185] studied the effect of ultrafine slag by partially substituting it for cement in high-strength concrete and evaluated the compressive strength and durability characteristics of hardened concrete.
3. *Natural and artificial pozzolan*: Materials of volcanic origin or industrial by-products with high pozzolanic properties, allowing them to replace clinker and reduce associated emissions. Pozzolan reacts with calcium hydroxide during cement hydration to form stable and strong compounds. *Mohsen et al.* [186] studied the effect of partial replacement of cement with fly ash and natural pozzolan by evaluating workability, mechanical and microstructural properties. *Presa et al.* [187] and *Sanjuán et al.* [188] evaluated the potential of volcanic ash as pozzolanic raw materials for the development of a possible sustainable cement. *Uluslu et al.* [10] and *Aydin and Baradan* [11] studied the effects of incorporating pumice rock into cement and cement mortars with reduced CO₂ emissions, respectively. No works have been found in the literature that directly refer to the use of volcanic lapillus; however, a few works have been found that mention the use of red and black pozzolans in the manufacture of mortars [189][190].
4. *Ground limestone*: It can be added to cement in small amounts to reduce the amount of clinker needed. While not as reactive as pozzolan or fly ash, limestone can improve some cement properties, such as workability. *Weiyang et al.* [191] evaluated the possible use of magnesite/limestone as a supplementary cementitious material by studying the hydration characteristics of ternary slag cement mixtures containing magnesite or limestone. *Ji et al.* [192] evaluated the hydration process and microstructural properties of cement containing limestone waste. *Jiang et al.* [193] studied the compressive

strength, pore microstructure and diffusion properties of chloride in Portland cement limestone paste with different percentages of limestone and different fineness levels.

5. *Metakaolin and calcined clays*: materials obtained from the controlled calcination of kaolin or other clay materials, which possess good pozzolanic properties contributing to the reduction of clinker in cements. *Qin et al.* [194] focused on the study of flowability, compressive strength, microstructure, phase change and heat of hydration of cement-based materials modified by calcined zeolite and montmorillonite. *Wu et al.* [195] improved the pozzolanic activity of low-grade natural sepiolite by calcination for use as SCM and evaluated its effects on hydration and compressive strength of cement. *Kuo et al.* [196] studied the strength and permeability of organo-modified montmorillonite-based cement mortars.

As for alternative cements, however, the most promising ones are:

1. *Limestone Calcined Clay*: calcined clay cement (LC3) is one of the recently developed ternary blend cements; it consists of a mixture of clinker, limestone, and calcined clay. LC3 can reduce CO₂ emissions by up to 40% because it is produced using low-quality limestone and clays that are available in large quantities and can replace clinker in very high amounts. The alumina from the calcined clay and carbonate from the limestone react with each other to promote the development of a finer microstructure, giving the cement excellent mechanical performance [197]. *Avet and Scrivener* evaluated the influence of the calcined kaolinite content of calcined clays on the hydration of LC3 containing 50% clinker (LC 3 -50) [198]. *Barbhuiya et al.* and *Sharma et al.* through a review paper provided a comprehensive analysis of the production, properties and applications of LC3 and also evaluated its importance in reducing carbon emissions in the cement industry [199][200]. *Muzenda et al.* studied the role of limestone and calcined clay on the rheological properties of LC3 [201].
2. *Geopolymer cements*: They are an innovative alternative that does not require the use of clinker. Derived from alkali-activated aluminosilicate materials, geopolymer cements promise a significant reduction in CO₂ emissions while maintaining good mechanical properties and durability. *Basquiroto de Souza et al.* [202] nano-engineered geopolymer cementitious materials to have a nacre-like microstructure in order to increase tensile/bending properties. *Saccani et al* [203] investigated the effect of glass in alkali activated mortars. *Stroscio et al.* [204] and *Barone et al.* [205] explored the possibility

of using Sicilian clay sediments as precursors to produce alkali-activated materials with properties comparable to commercial building materials. *Rashad et al.* [206] investigated the influence of using natural basalt mixed with fly ash to make geopolymeric cement cured in air and water on flowability, compressive strength, microstructure, hydration products and resistance to environmental conditions. *Altimari et al.* [32] studied the use of volcanic raw materials of volcanic in order to obtain alkaline-activated materials. *Capasso et al.* published a review regarding the use of different types of soil waste to produce geopolymeric binders [207].

Although significant efforts are underway to reduce CO₂ emissions, it will still be difficult to balance this with the cement production required to meet global demand. Emission intensity in cement production has increased since 2015, largely due to an increase in the clinker-to-cement ratio, although the rate of growth has slowed recently. The main strategies for reducing carbon emissions in the sector include improving energy efficiency, adopting low-carbon fuels, optimizing material use and developing innovative near-zero-emission technologies. The last two approaches are particularly effective in contributing to direct emission reductions under the Net Zero scenario. To align with this scenario, it will be necessary to develop and implement new technologies that are not yet available. In the context of the ‘Zero Emissions by 2050’ scenario, global cement production will remain relatively stable until 2030. The adoption of material efficiency strategies, aimed at optimizing the use of cement along the construction value chain, can also contribute to reducing demand and, consequently, the sector's CO₂ emissions. In addition, carbon capture and storage (CCS) is set to play a key role in the decarbonization of cement, while alternatives such as the use of clinker derived from non-carbon sources could enable the elimination of upstream emissions [208][209].

The literature is really extensive regarding the challenges of making cement production sustainable, but despite everything we are not aware of any cement mortars containing volcanic lapillus as SCMs have been studied.

3.2 PART 1 – VOLCANIC LAPILLUS AS SUPPLEMENTARY CEMENTITIOUS MATERIAL

3.2.1 RAW MATERIALS AND SAMPLES PREPARATION

The raw materials used in this study were as follows:

- CEM I 52,5 R, type I Portland cement with very high normalized strength and high initial strength;
- Limestone Portland cement (CEM II/B-LL 42.5 R) containing 65%-79% clinker, 21%-35% limestone;
- CEN certified, EN196-1 and ISO 679:2009 compliant normalized sand;
- Volcanic lapillus scrap, described in Chapter 1, which were initially less than 3 mm in diameter, were ground to an average particle diameter of less than 100 μm in order to increase their reactivity and compatibility with clinker;
- Tap water.

The raw materials were mixed by initially placing the solid parts in an automatic mixer for 30 seconds (E094, Matest). Then water was added, and the mixture was stirred for about 3 minutes. The resulting fresh mortars were poured into molds measuring 40 mm $\times$ 40 mm $\times$ 160 mm and compacted using a shake table (Model 64-L0038/A, Controls). The samples were then placed in a curing chamber maintained at a temperature of $20\pm 1^\circ\text{C}$ and 90% relative humidity. The samples were first allowed to cure in the climate chamber for a period of 2, 5, 21 and 28 days, corresponding to the total curing periods of 2, 7, 28 and 60 days, respectively. Temperature and humidity in environmental conditions were used for the remaining of the curing period.

Ten compositions were studied, five based on CEM II and five based on CEM I (Compositions (1-5) and (6-10) respectively in **Table 3.2**). Mixtures 1 and 6 are classic cement mortars composed of water, cement and sand in a 1:2:6 ratio, while mixtures 2-5 and 7-10 have partial cement substitution between 5-20%.

Table 3.2. Mixing ratios for the production of cement mortars. The first column (1-5) refers to samples manufactured with CEM II, while the second column (6-10) refers to samples manufactured with CEM I.

		Water (g)	Cement (g) CEM I or CEM II	Sand (g)	Lapillus (g)	% Replacement
1	6	225	450	1350	-	0%
2	7	225	427.5	1350	22.5	5%
3	8	225	405	1350	45	10%
4	9	225	382.5	1350	67.5	15%
5	10	225	360	1350	90	20%

Note: Limestone Portland cement was chosen because the production of CEM II in Italy is about 75% and, within this category, C₃A Portland limestone accounts for 65% [210].

3.2.2 METHODS

The samples were subjected to different analyses, including spreading test, determination of bulk and true density, compressive strength test, microstructural analysis, evaluation of ASR reactivity, measurement of chloride and sulfate penetration, capillary water absorption, and quantification of calcium hydroxide by TGA.

The consistency of fresh cement mortar is used to understand the workability of the paste and provides indications of its viscosity. This consistency is determined by measuring the spread. Fresh mortar was poured inside a standard-sized metal cone (lower inside diameter of 100 mm, upper inside diameter of 70 mm, and height of 60 mm) placed on a shake table (Model 64-L0038/A, Controls) and then 15 blows, called settling blows, were given, useful for measuring static flow. Then another 15 shocks were given, in about 15 seconds, in accordance with UNI EN 413-2:2016, to determine the dynamic flow, which is of greater interest because it more accurately simulates the setting conditions [211].

Spreading is expressed as the difference between the obtained diameter (slump) and the lower inner diameter of the cone:

$$\text{Spreading [mm]} = \text{Slump diameter [mm]} - \text{Cone diameter [mm]}$$

For the purpose of good workability, it is necessary to adopt a spread of cement mortar between 140 mm and 200 mm (with a tolerance of ± 10 mm), as prescribed by UNI EN 1015-2:2007.

The geometric or bulk density has been calculated as the ratio between the mass (weight of the sample after curing) and the volume of the sample, calculated also considering the porosity, as described in UNI EN 1015-6:2007. The true density was measured as described in *section 1.4.1*. In both measurements, the volume considered was equal to that of a prism with dimensions 40x40x160 mm, i.e. 256 cm³.

The compressive strength was performed on mortar samples that had been cured for 2, 7, 28 and 60 days, according to the test methods reported in standard UNI EN 196-1:2016. The sample was placed on a designated surface with a 40x40 mm section and subjected to compression by means of a load perpendicular to the support surface, exerted by a hydraulic press, with a gradual progression so that the deformations of the material could be recorded. The tests were performed with a 15/250 kN automatic compression testing machine (Controls, L1052).

Microstructural analysis performed by SEM was described in *section 1.4.1*. The analyzed samples, after being brought to an appropriate size (<1 cm per side), were placed on an aluminum stub by means of a silver-based glue and finally were metallized with a gold layer of few nanometers to make the sample conductive.

The influence of lapillus on the ASR reactivity was investigated by an accelerated test partially conforming to the ASTM 1260 Standard. Samples 25 x 25 x 280 mm were cast and immersed in a 0.1 N NaOH solution at 80°C after a 24 h conditioning in water at the same temperature. The dimensional changes were recorded up to 16 days of curing. As a reactive aggregate, discarded lamp glass has been used. This glass composition has been selected on account of its extremely high reactivity towards alkali [212].

Cement contains small amounts of alkali (Na₂O and K₂O), which on hydration pass into solution in the form of hydroxides. Reactive aggregates react with hydroxyl ions (OH⁻). A gel of alkaline silicates forms on the surface of the granules, which absorbs water and increases in volume, developing pressure between the granules and cement paste. This is a slow process and expansion occurs during hardening: the increase in intergranular pressure can result in localized

swelling and cracking in the concrete. For this reason, this test was performed to assess whether the matrix containing lapillus in the presence of alkali can give expansion.

Chloride penetration was investigated according to UNI 11747 Standard. The effects of sulphates diffusion on the mortars were investigated by ASTM C1012 Standard, i.e. by immersing the specimens in a Na₂SO₄ solution and evaluating their expansion of up to 15 weeks of curing in order to evaluate the effects of the SCM on the formation of expanding products.

To measure the water absorption after 28 days of curing, a capillary test (EN 15801 [**]) was performed using three cylindrical samples with a 25 mm radius and 55 mm height. The amount of water absorbed was calculated according to the following equation:

$$Q_i = (m_i - m_0)/A$$

where Q_i is the amount of absorbed water at time t_i (kg/m²), m_i is the weight of the sample at time t_i (kg), m_0 is the weight of the dried sample (kg), and A is the absorption area in contact with water (m²).

In order to determine the amount of calcium hydroxide in the different mixtures at different curing times, pastes were mixed according to **Table 3.2**, without adding the normalized sand, and kept in a water saturated tank at 20 ± 1 °C. At scheduled times (28 and 90 days), samples were manually milled in a mortar and the powders sieved below 150 μ m. The sieved powders were heated from 30 to 800 °C (20 °C/min rate) by means of a TA Q50 Thermogravimetric Analysis, in nitrogen flow (60 mL/min). The amount of calcium hydroxide was evaluated by determining the weight loss from 450 to 550 °C.

3.3 RESULTS AND DISCUSSION

3.3.1 SPREADING TEST, BULK AND TRUE DENSITY, COMPRESSIVE STRENGTH

The spreading test was carried out on the samples of mortars produced with both CEM II 42.5 and CEM I 52.5 in order to evaluate the workability of the pastes and, if necessary, the addition of fluidizing additives. The values shown in **Figure 3.1** are the averages of the results obtained for each sample; each test was performed 4 times.

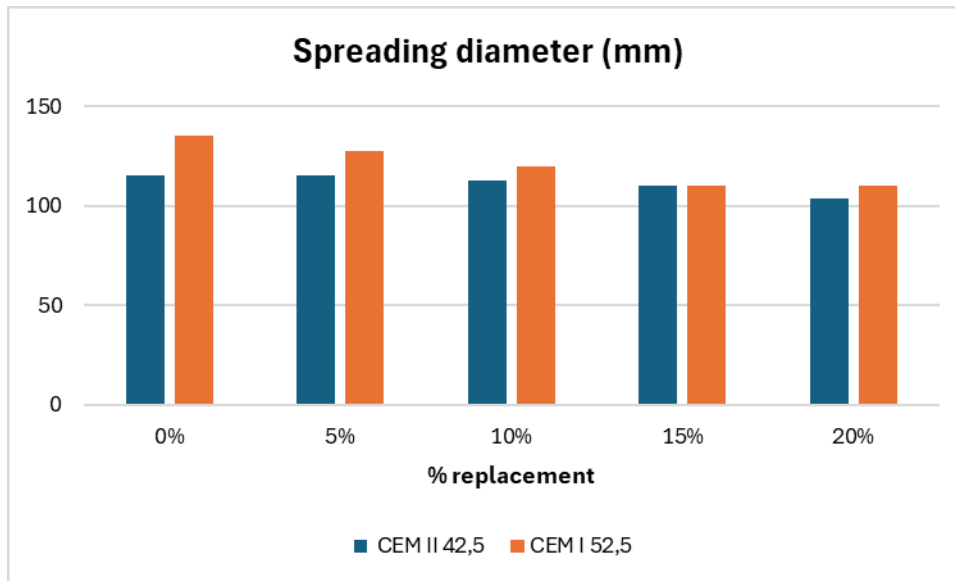


Figure 3.1. Spreading test performed on samples. Blue histograms are related to cementitious mortar manufactured with CEM II 42,5 while orange histograms are related to the use of CEM I 52,5. The standard deviation associated with mortars manufactured with CEM I is ± 15 mm while that associated with mortars manufactured with CEM II is ± 8 mm.

The trend of the spreadability measure, considering both types of samples, shows decreasing values. The values obtained decreased linearly as the percentage of lapillus increases; the value obtained is similar to the reference value up to the 10% lapillus of replacement; with the 15% replacement it decreases more, but the value can still be considered acceptable when compared to the reference sample. With the 20% lapillus replacement, the value decreases significantly with respect to the spreading measure, which results in a low workability of the paste. The comments reported above are relative to CEM II 42.5. If it considers the data obtained from the samples made with CEM I 52.5, it is possible to see that the decrease in values is more pronounced among the samples and starts already with the addition of 5%. For this reason, probably already starting from 10% replacement, it may be necessary to add small percentages of fluidizer. Volcanic lapillus, due to its porosity [143], tends to absorb a lot of water, making the mixture more viscous, since the fraction of water absorbed by the cement turns out to be less, so that the use of additives may be necessary.

The geometric or bulk density was calculated a few minutes after casting the samples in the mould, after 2 days of curing and 28 days of curing.. This measurement was made because lapillus, being less dense than cement, should contribute to the lightening of the material. The aim is to check whether this lightening is maintained even after a longer curing period.

In **Figure 3.2**, it is possible to observe the trend of the average geometric density of the fresh-cast samples and cured samples, relative to 4 measurements per sample, as a function of the

change in the percentage of lapillus replacement. In the case of fresh samples, it can be observed that the higher the percentage of lapillus inserted into the sample, the lower the density value, i.e. the material becomes lighter. Considering the samples made with CEM II 42.5, it is possible to say that: fresh samples showed values of apparent density between 2.07-2.17 g/cm³ for the reference sample and the one with 20% lapillus respectively. Samples 2-days-cured and 28-days-cured showed a decreasing trend when increasing curing time. In general, the density decreases by about 1.9-2.8% after 28 days. With regard to the samples made with CEM I 52.5, it is possible to say that: fresh cast samples showed apparent density values between 2.21-2.16 g/cm³ for the sample without substitution and the one with 20% lapillus respectively, showing a slightly higher density than the previous samples. The samples cured for 2 and 28 days also showed a decreasing trend with increasing ageing time. If we compare the values obtained with the fresh cast samples and those cured for 28 days, we can observe a decrease in density ranging from 3.2 to 6%, with the maximum value recorded with the 20% lapillus substitution.

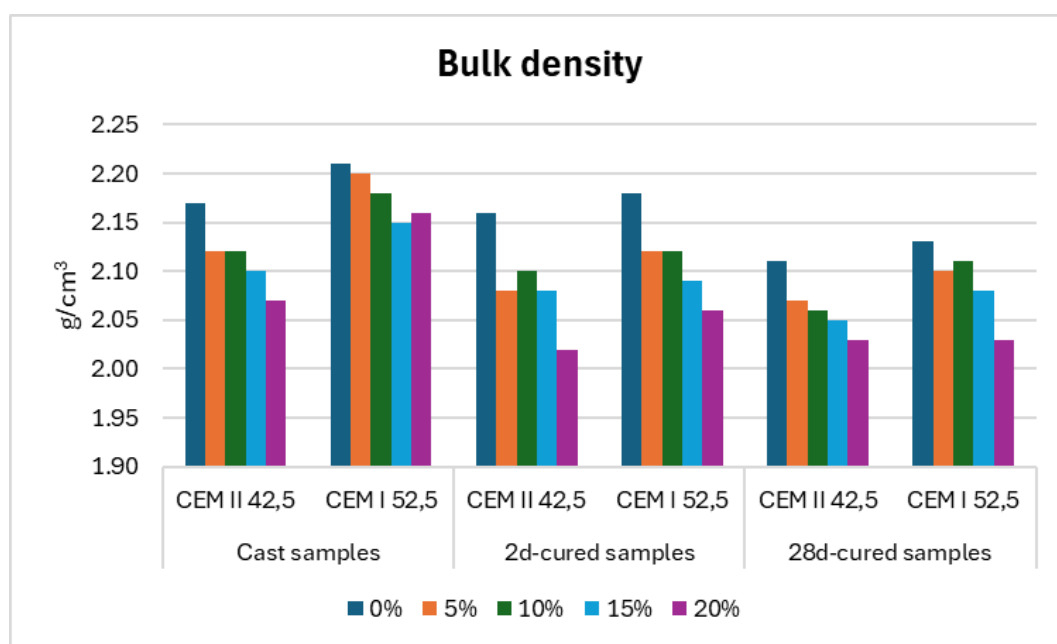


Figure 3.2. Bulk density of just cast samples and cured samples.

The real density was measured on the reference sample and on samples containing 5% and 20% volcanic lapillus respectively after a curing time of 28 days. The values obtained are not very different from each other, both in the case of samples manufactured from CEM II and CEM I, ranging between 2.6-2.7 g/cm³, although the real density increases as the percentage of lapillus increases. This could be due to the percentage of Fe contained in lapillus, but also to the fact

that this value takes the density into account regardless of the presence of porosity; although the density of lapillus is lower than that of cement, due to hydration reactions and the long curing time, the real density increases, making it possible to have a material with a high mass in a small volume, while remaining a lighter material than a standard mortar.

The compressive strengths of the mortars produced are shown in **Figure 3.3**.

It can be seen that for all the compositions there is an increase in the compressive strength as the curing time increases; at the same time, however, it can be seen that as the percentage of lapillus used in the samples increases, the mechanical strength slightly decrease up to 10% of lapillus addition, while for higher percentage (15%, 20%) the decrease is more significant: lapillus is a material that can be less efficient than cement under loading conditions, so it is not advisable to replace it in high percentages. The above result is consistent with the data reported in the literature on the substitution of raw materials of volcanic origin for the production of mortars or blended cements: compressive strengths tend to decrease as the percentage of substitution increases. This could be due to the fact that cement hydration tends to be delayed as the lapillus content increases and that the active material in silicon and aluminium is lower than in reference sample [61][188][212][213]. In any case, it should be noted that blended cements tend to increase their mechanical strength in the long term due to pozzolanic behavior [214][215][216].

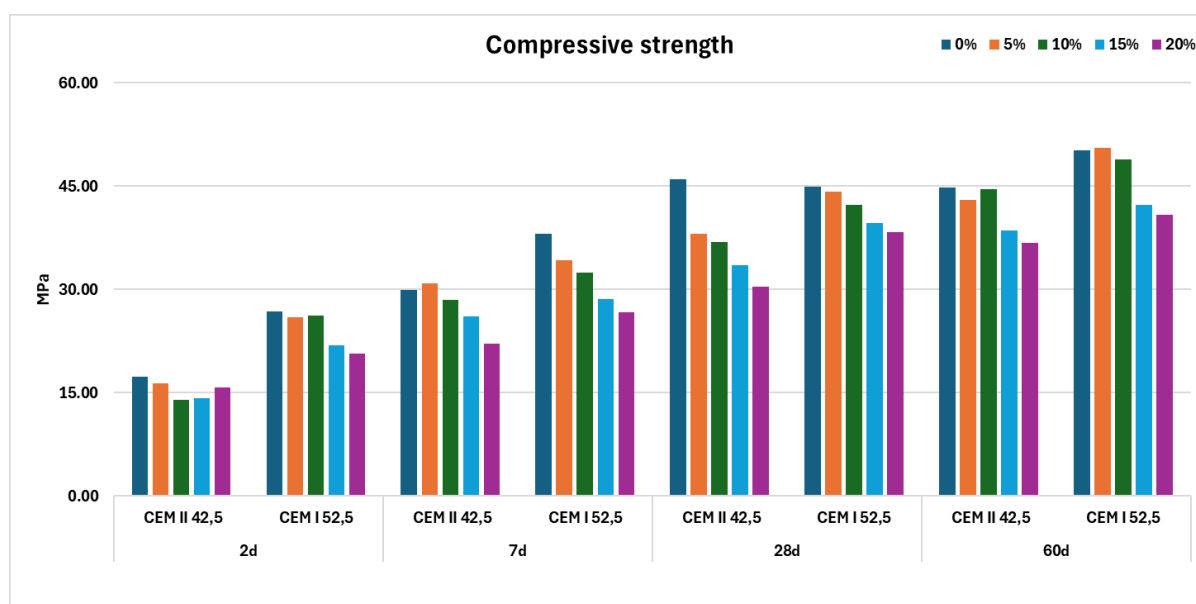


Figure 3.3. Compressive strength at different curing time of two groups of formulations.

Table 3.3. Standard deviation related to data reported in **Figure 3.3**.

CEM II 42,5 std_dev						CEM I 52,5 std_dev					
	0%	5%	10%	15%	20%		0%	5%	10%	15%	20%
2d	1.24	2.42	1.43	1.63	1.63	2d	3.00	0.96	1.53	1.65	1.39
7d	4.79	2.21	2.00	1.39	1.04	7d	3.37	1.26	2.44	0.70	1.77
28d	2.98	4.30	1.01	1.33	1.39	28d	2.08	4.06	2.53	1.56	2.41
60d	4.49	3.06	2.76	4.19	3.27	60d	3.13	5.26	1.68	3.72	1.83

For long curing times there is an increase in compressive strengths even in samples containing 20% lapillus; for shorter times, however, the maximum tolerable replacement percentage is around 15%. At 10% it is close to the value of 42.5 MPa or 52.5 MPa, while at higher percentages it tends to be close to the value of the lower resistance class. It should be noted that the uncertainty, and therefore the standard deviation (reported in **Table 3.3**), increases as the curing time increases, thus increasing the variability of the data in the long term.

3.3.2 MICROSTRUCTURAL ANALYSIS

The observation of the samples using a scanning electron microscope (SEM) was carried out in order to provide information on the degree of compaction of the samples. This analysis was performed only on samples manufactured with CEM II 42,5. This technique allows the microstructure of the samples to be investigated and the type and shape of the components to be assessed, in particular the formation of gel, which provides information on the degree of reaction of the hydrated compounds. SEM analysis was conducted on reference samples and the one containing 20% of lapillus cured for 2 and 28 days to highlight the progress of hydration reactions. All images presented below were acquired in backscattered electron mode.

Observing the two-day cured reference sample in **Figure 3.4**, it can be seen that the matrix is not compact, due to the short curing time but observing at a magnification of 300x (**Figure 3.4 right**) a good adhesion of the gel-aggregate interface can be observed, even if there are areas where the gel is firmly attached to the granules (1) and others where this adhesion is less marked (2).

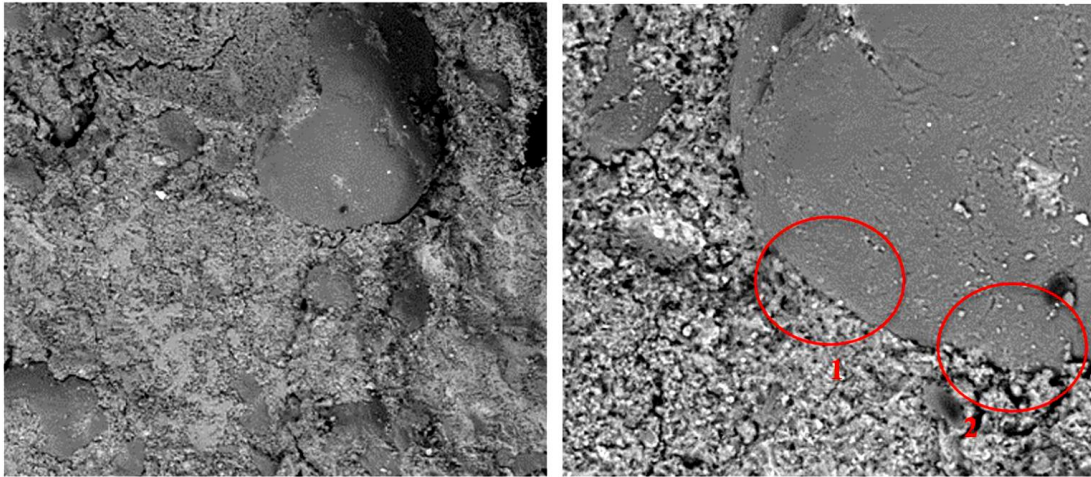


Figure 3.4. SEM images of the 2-day aged reference sample at 80x (left) and 300x (right).

Higher magnification (1200x) in **Figure 3.5left**, shows the presence of needles, approximately 25-30 μm in size, consisting almost entirely of calcium and oxygen (50.74% and 44.71% respectively), probably Portlandite $\text{Ca}(\text{OH})_2$ resulting from the hydration of the cement and representing the beginning of the hardening phase. In **Figure 3.5 right**, on the other hand, the formation of cement gel can be seen, indicating that hydration processes are underway.

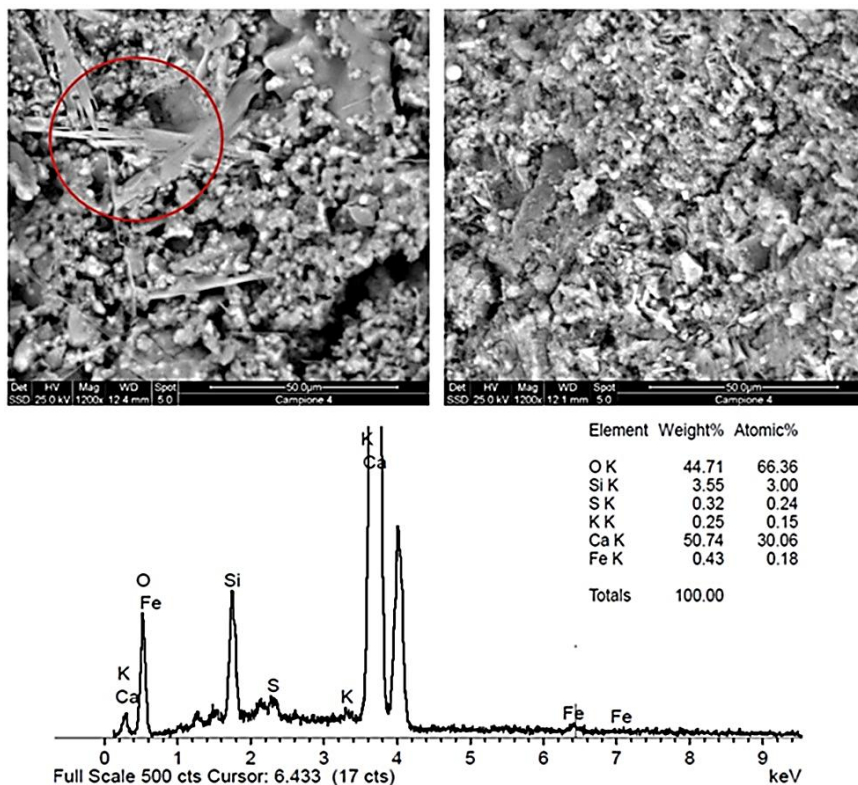


Figure 3.5. SEM images of the 2-day aged reference sample of needles (left) and gel (right) at 1200x magnification and the eds spectrum at the highlighted area (needle).

Comparing sample 1 with sample 5, i.e. the sample containing 20% lapillus instead of 100% cement, it can be observed that the sample containing lapillus presents a less dense structure (**Figure 3.6**), in which granular regions can be discerned, which are clearly visible in the 300x magnification image (**Figure 3.6 right**). However, the gel-aggregate adhesion appears to be satisfying given the short maturation period.

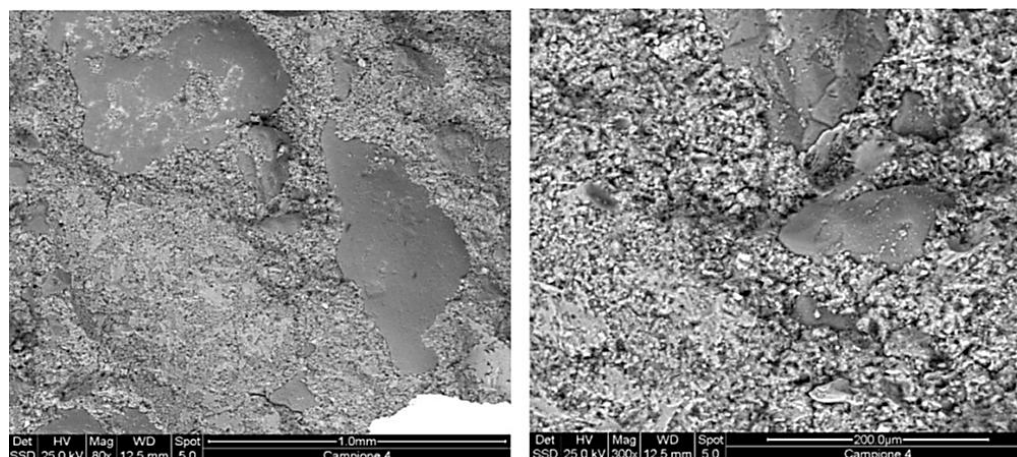


Figure 3.6. SEM images of sample 5 aged 2 days at 80x (left) and 300x (right).

In micrograph with magnification of 1200x, **Figure 3.7**, it is possible to identify areas that are more compact and areas with a more granular surface. In the former case, this could be an area free of lapillus, as the percentage composition consists entirely of calcium and small percentages of other components (**Figure 3.7**, right-hand side). It is also possible to distinguish a white granule (3) of the order of 6-7 µm consisting of 29% calcium and 12% silicon, the composition and size of which make it similar to a grain of unreacted clinker (C_2S - C_3S).

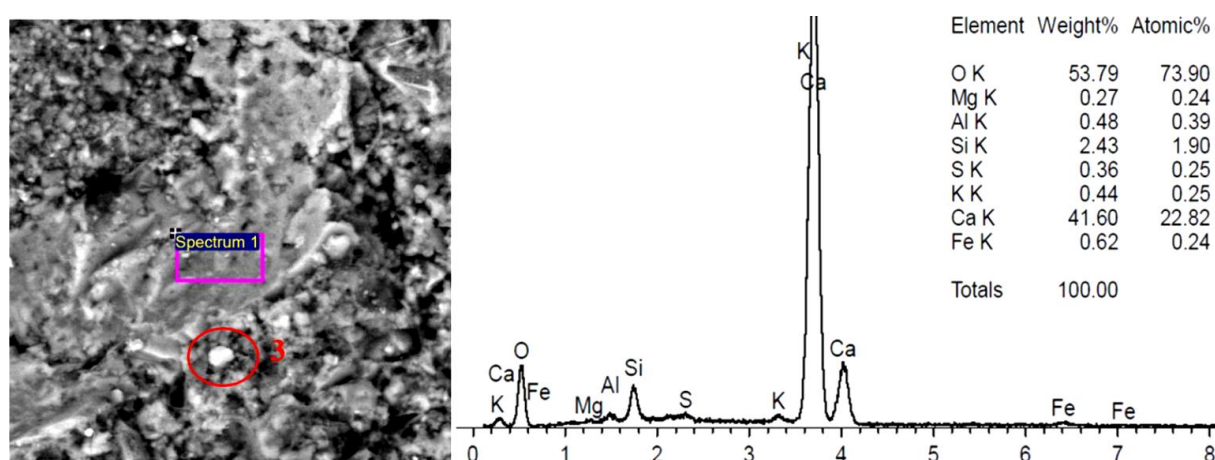


Figure 3.7. SEM image at 1200x (left) and eds spectrum (right) of sample 5 cured 2 days.

SEM images in **Figure 3.7** and **Figure 3.8** show the same area, but the portion relating to the EDS analysis changes. In the more granular region, **Figure 3.8**, it is possible to identify areas with a higher concentration of iron, in fact, from the spectrum it can be seen that the Ca/Si ratio is approximately 6 and that there is an increase in the content of iron (1.46%), potassium and magnesium (2.60% and 1.15% respectively) compared to the EDS analysis of the previous region, these being the elements that characterize the composition of lapillus after silicon and aluminum (Fe 9.15%, Ca 9.27%, Mg 4.25% and K 3.66%), which are also present in large quantities in the cement powder.

The sample containing 20% lapillus is characterized by two different types of gel (one related to chemical analysis of spectrum 1 and one related to chemical analysis of spectrum 2), since they have the same elements but in different proportions. In any case, it is not possible to clearly discern the presence of lapillus in the form of grains, since it reacted within the mixture to form cement gel.

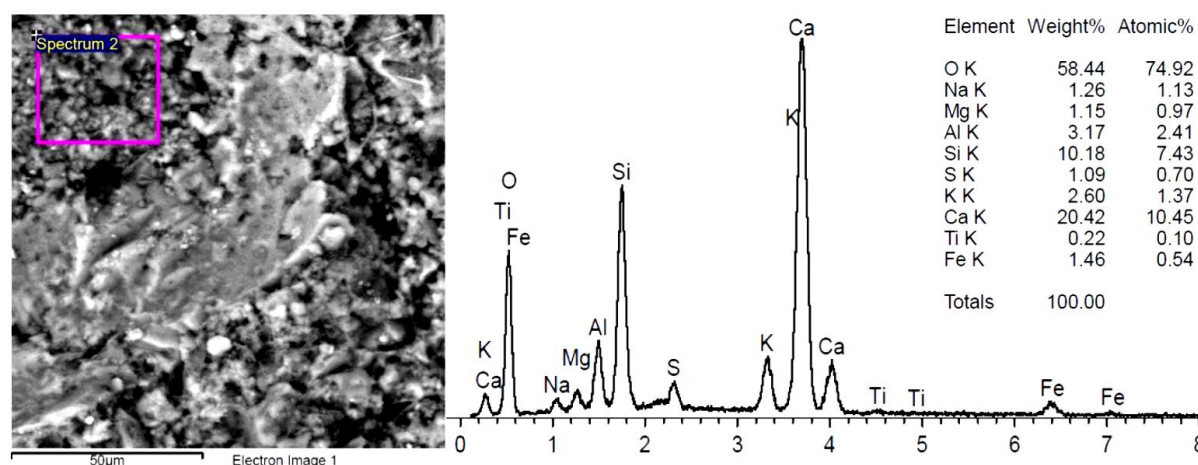


Figure 3.8. SEM image at 1200x (left) and spectrum (right) of sample 5 aged 2 days.

Looking at the 28-day ageing time, we can see a change in the microstructure compared to the previous cases. The reference sample aged for 28 days is already much denser, with good gel-aggregate adhesion and less porosity, as can be seen in **Figure 3.9**. It can also be seen that the number and size of the pores decrease with increasing curing time.

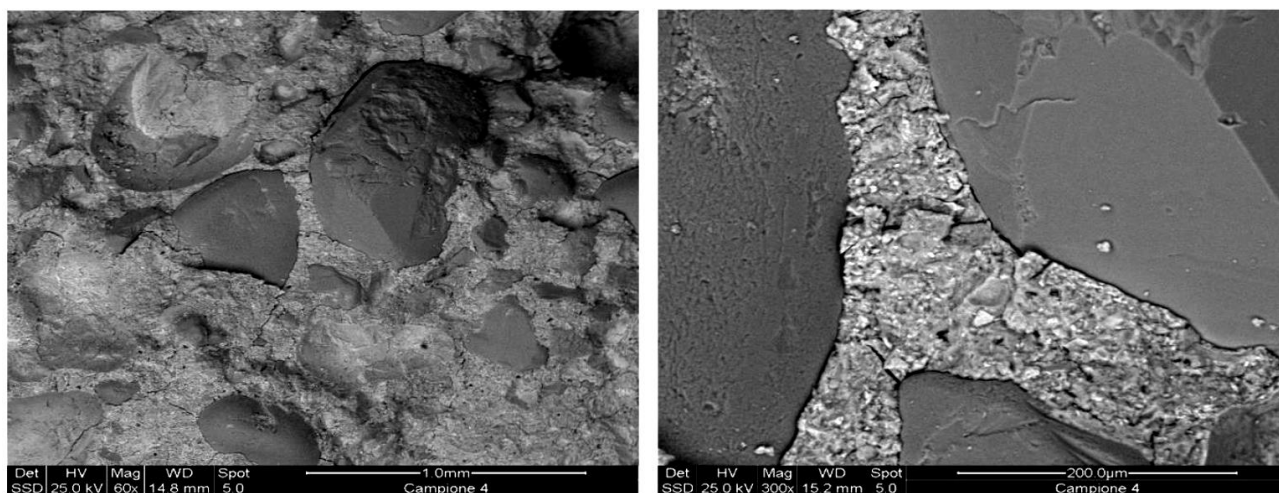


Figure 3.9. SEM images of the 28-day mature reference sample at 60x (left) and 300x (right).

The sample with a higher percentage of lapillus, aged 28 days, although has a lower compressive strength than the reference, as seen above, it is very dense, homogeneous and well bonded to the sand grains, compared to the sample aged 2 days, as shown in **Figure 3.10**. Also in this case, it is possible to observe a decrease in the porosity, both in terms of number and size, with an increase in the curing time.

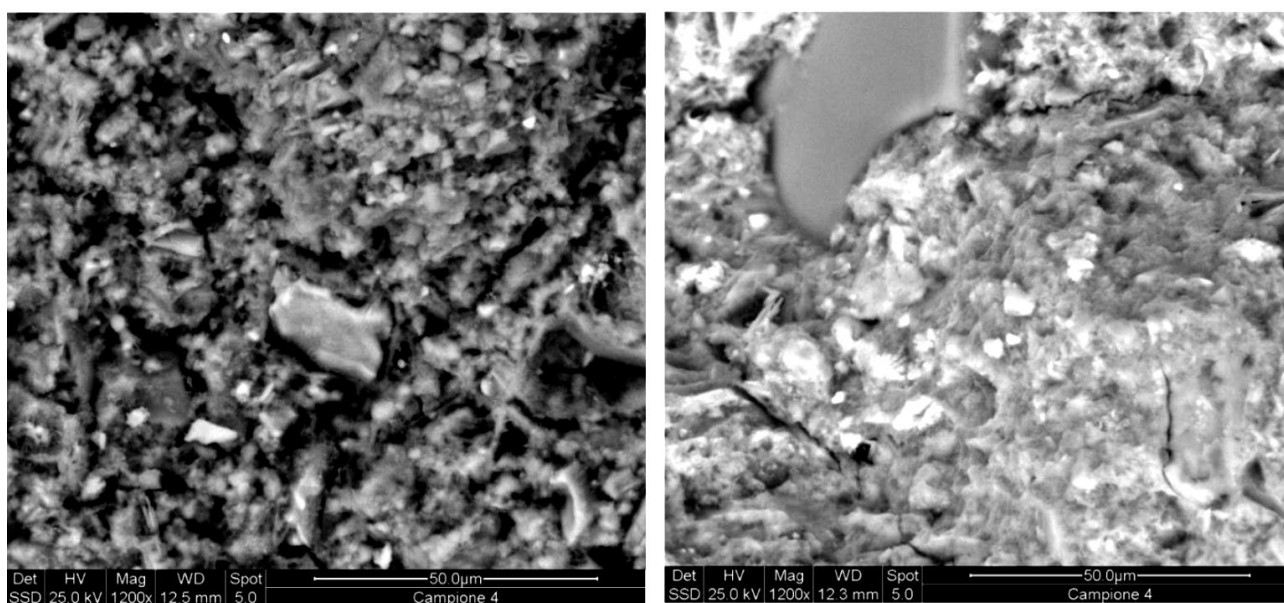


Figure 3.10. SEM images of the sample containing 20% lapillus at 1200x, 2 days cured (left) and 28 days cured (right).

3.3.3 ASR REACTIVITY, CHLORIDE AND SULPHATES PENETRATION, WATER ABSORPTION BY CAPILLARITY, CALCIUM HYDROXIDE CONTENT BY THERMOGRAVIMETRIC ANALYSIS

Figure 3.11 shows the results of the accelerated ASR tests. As can be observed, according to the high aggregates reactivity, the limit of 0.1 % is exceeded after a few days, but the rate and extent of expansion is slowed down and progressively decreased by the presence of lapillus. This effect is common to many others SCM already tested. The origin of the effect is still not completely understood, and many theories have been proposed. In this case, we can propose a mitigation effect deriving from the reduced calcium amount deriving from the pozzolanic reaction.

The intention was to emphasize the expansion, so discarded lamps glass was used, which has a very high reactivity to alkali. After 16 days, the sample with 10% of lapillus showed a 20% decrease in the expansion rate if compared to the reference sample, while that containing 15% of lapillus showed a 28% decrease.

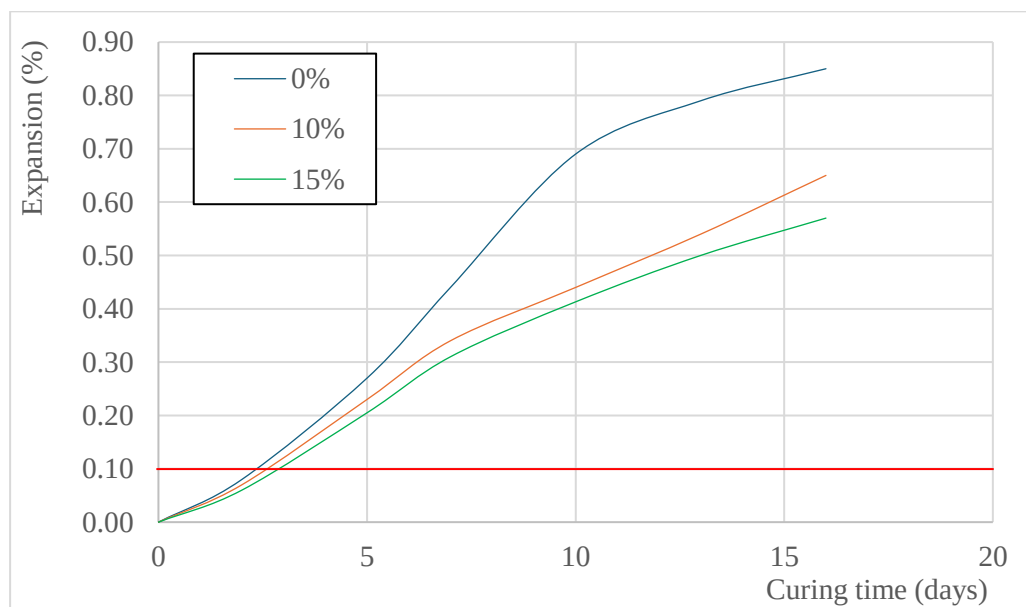


Figure 3.11. Expansion deriving from the alkali-silica reaction.

Moreover, **Figure 3.12** summarizes the results of the sulfates and chloride penetration tests. After 15 weeks of curing in the sulfate's solution, the dimensional changes of the unmodified mortar related to the formation of expanding products is still low, but it is higher than that found in mortars containing lapillus. As to the chloride penetration, the unmodified and 10% lapillus mortars behave in the same way as the reference mortar, while a deeper penetration takes place in the 15% sample. There are no reference values, but it is possible to say that there is not a particularly significant difference, and as discussed it may be due to the fact that at these maturities the sample containing 15% lapillus is still more porous than the reference.

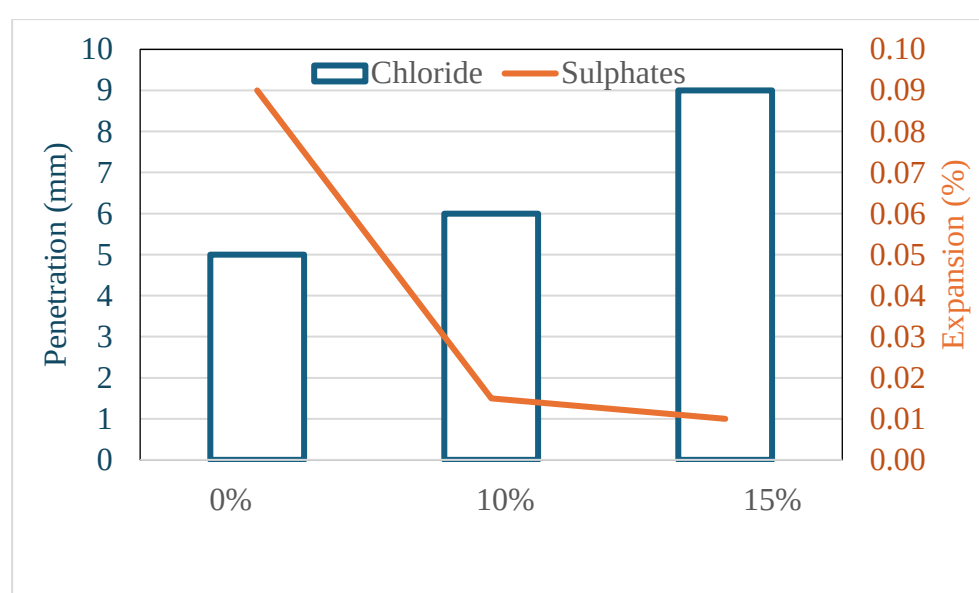


Figure 3.12. Chlorides penetration and expansion due to sulphates effects in mortars containing 0-10 and 15% of lapillus as SCM..

The experimental results of the water absorption permeation by capillarity (**Figure 3.13**) disclose a quite similar linear trend for all materials, but the 15% sample has a higher rate of permeation. This feature could explain the results found for chloride penetration. In the case of sulfates, the damage is related to the interaction between the diffused anions and the aluminates present in the mortars, which corresponds to the chemical reaction for the formation of ettringite, while in the case of chlorides ion the penetration depth is only related to the microstructure therefore to the physical percolation, due to the increase of porosity in the lapillus-based samples.

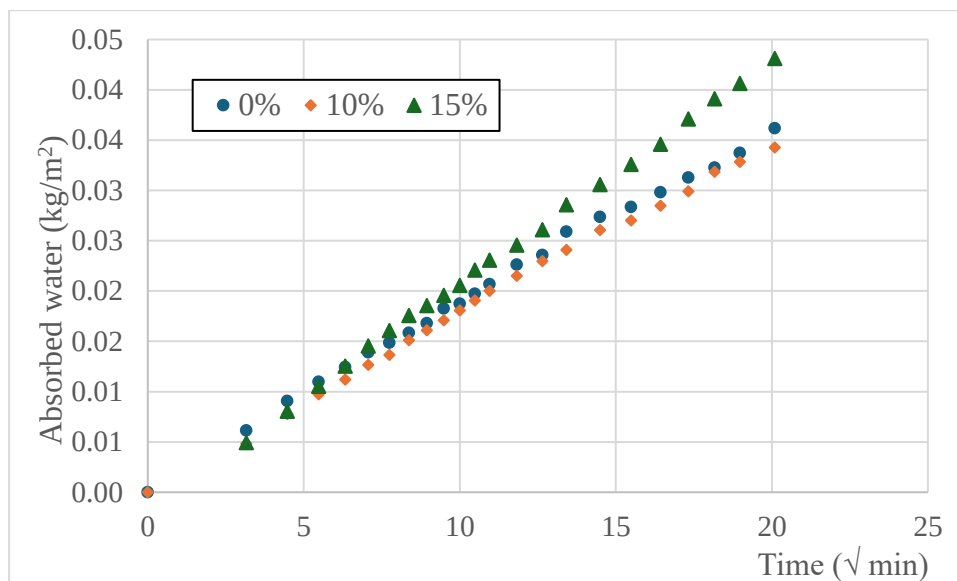


Figure 3.13. Water absorption by capillarity. The Circle refers to the reference; the rhombus and triangle refer to mortars containing 10% and 15% of lapillus as SCM, respectively.

In **Figure 3.14** the amount of calcium hydroxide detected in different pastes at different curing time, is summarized. As expected, modified sample contain less calcium hydroxide than the plain Portland one and the difference exceeds the one caused by C_3S and C_2S lower amount. Moreover, the difference increases as curing proceeds from 28 to 90 days. At 90 days there is still a fraction of calcium hydroxide both in 10 and 15% lapillus samples, a feature that can hint to a further pozzolanic reaction taking place at longer curing times.

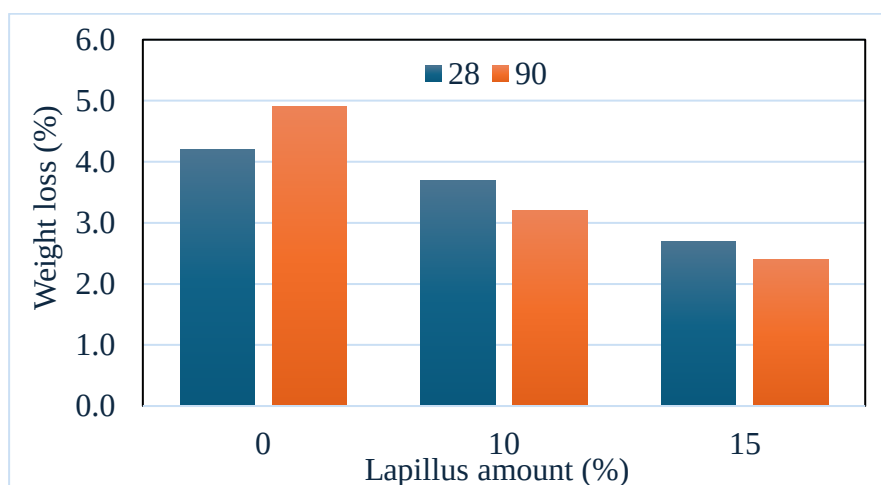


Figure 3.14. Weight loss from calcium hydroxide decomposition at different curing-times detected by TGA.

According to the experimental results lapillus behaves as many of the investigated SCM in literature. The addition decreases the damage induced by sulphates diffusion [217][218][219][220] and the tendency to develop ASR reactions [221][222][223]. The precise mechanisms, though which SCM in general provide these benefits, have not been completely understood and are still a matter of discussion. Concerning the present research, what can be underlined is the progressive reduction in the amount of calcium hydroxide available for possible degrading reactions, as confirmed by TGA analysis. As to the overall amounts of aluminum oxides that play a negative role in sulphates degradation, in the 10 and 15% samples, on account of the low amount of the amorphous dissolvable phase in lapillus, an overall lower amount of Al_2O_3 is predictable. This feature and the lower calcium content already underlined can explain the higher stability of the modified mortars to the sulphate's diffusion. However, the rate of diffusion of chlorides is slightly faster than the one in the unmodified mortars, a feature that supports a higher porosity of the matrix reflected by the lower mechanical properties at 15% substitution.

3.4 PART 2 – VOLCANIC LAPILLUS AS AGGREGATE

3.4.1 RAW MATERIALS AND SAMPLES PREPARATION

The raw materials used in this study were the same described in section 3.2.1 with the exception of CEM I 52,5 R, which was not used¹. In this case, volcanic lapillus replaced fine aggregate, thus normalized sand. To replace it, it was necessary to reconstruct with lapillus the grain size curve of normalized sand. The particle size distribution is of great importance because sand is the component that provides mechanical strength to the mortar.

The preparation of mortar samples is described in *section 3.2.1*. The compositions made are shown in **Table 3.4**. Mixture 11 is a classic cement mortar composed of water, cement and sand in a 1:2:6 ratio, while in mixtures 12-15 the normalized sand has been replaced by lapillus in percentages between 5-20%.

¹ The experiment began with CEM II, and given the results obtained, it was decided not to replicate the study with CEM I.

Table 3.4. *Mixing ratios for the production of cement mortars.*

	Water (g)	Cement (g)	Sand (g)	Lapillus (g)	% Replacement
	CEM II				
11	225	450	1350	-	0%
12	225	450	1282.5	67.5	5%
13	225	450	1215	135	10%
14	225	450	1147	202.5	15%
15	225	450	1080	270	20%

The resulting mixture was not very workable due to the high-water absorption of lapillus, so the volcanic lapillus was saturated by soaking in water for 24 hours before use. After 24 hours, the unabsorbed water was removed, the lapillus was set to air for 1 hour, buffered, and mixed with the other raw materials to make mortars.

3.4.2 METHODS

The sample described were subjected to spreading test, determination of bulk and true density, compressive strength test and microstructural analysis. All analyses were described in *section 3.2.2*.

3.5 RESULTS AND DISCUSSION

3.5.1 SPREADING TEST, BULK AND TRUE DENSITY, COMPRESSIVE STRENGTH

The spreading test was carried out on samples of mortars produced by replacing standard sand with lapillus to assess the workability of the pastes. The average values obtained are shown in **Figure 3.15**.

The spread measure shows increasing values, the values obtained increase linearly with the increase in the percentage of lapillus in substitution of sand.

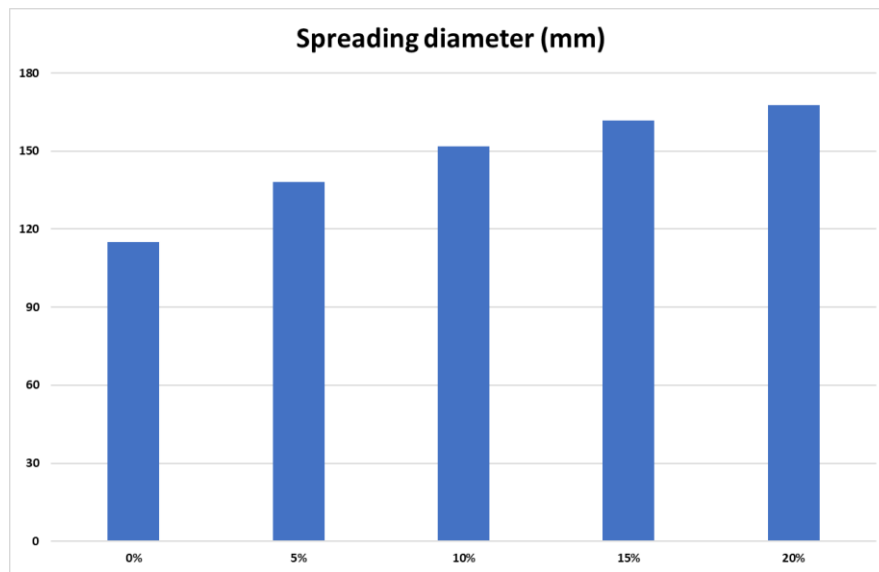


Figure 3.15. Spreading test performed on samples.

Comparing the results obtained with those reported in *section 3.3.1*, it is possible to see that the trend is completely opposite. This phenomenon is due to the percentage of volcanic lapillus that replaces sand, since it has the opposite behavior to sand: sand does not absorb a large amount of water, while lapillus, thanks to its intrinsic porosity, can absorb high amounts of water, making the sample much more fluid and therefore workable. On the other hand, a high percentage of lapillus tends to make the paste too fluid, with the risk of prolonging the maturation time.

The trend of the mean density of just cast samples and 7 days cured samples is shown in **Figure 3.16**.

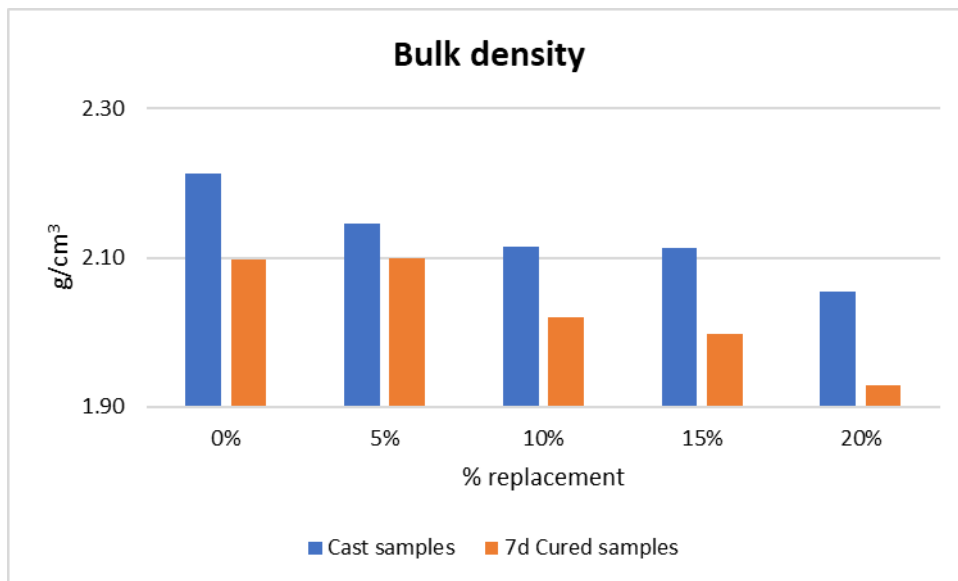


Figure 3.16. Bulk density of just cast samples and 7 days cured samples.

As the amount of lapillus in the mixture increases, the density of the just cast samples decreases from a reference value of 2.21 g/cm³ to 2.05 g/cm³ for a sample containing 20% lapillus. It is interesting to note that after 7 days the apparent density is much lower than that measured on the fresh cast samples, which could be due to the greater amount of water absorbed by the mixtures containing lapillus, as mentioned above. Some of the water absorbed during the ageing process evaporates, reducing the mass of the sample and consequently its density.

With regard to the true density of the samples, it can be seen in **Figure 3.17** that the trend of the values measured after 28 days of curing is constant and does not affect the substitution rates.

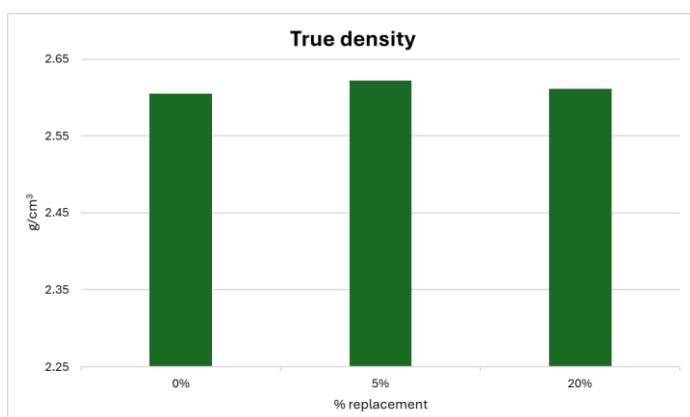


Figure 3.17. True density of 28 days cured samples.

This suggests that for long ageing periods, which allow greater compaction of the material, the true density, without considering the presence of porosity, remains almost unchanged.

Compressive strength of mortar manufactured is shown in **Figure 3.18**.

It can be seen that the compressive strength of all the compositions increases as the curing time increases, but at the same time it can be seen that as the percentage of lapillus in the mixture increases, the mechanical strength decreases significantly, even for very low replacement (5%). The compressive strength of the samples in which the sand was replaced by lapillus, after two days of curing, showed lower values between 77-87% than the reference; these values depend on the sample considered. This variation is a little more limited in samples which have reached 28 days of curing, for example if it compare with the reference compressive strength is possible say that: the sample containing 5% lapillus had a decrease in compressive strength of 38% compared to 77% of the same sample at 2 days of curing, while the sample containing 20% lapillus has gone from values lower than 87% at 2 days of curing to values lower than 52% at 28 days.

This is probably due to the high-water content that lapillus tends to absorb during mixing. This is released more slowly and does not allow complete setting in the conventional times for a standard mortar. Longer curing times would probably still give better results than those obtained.

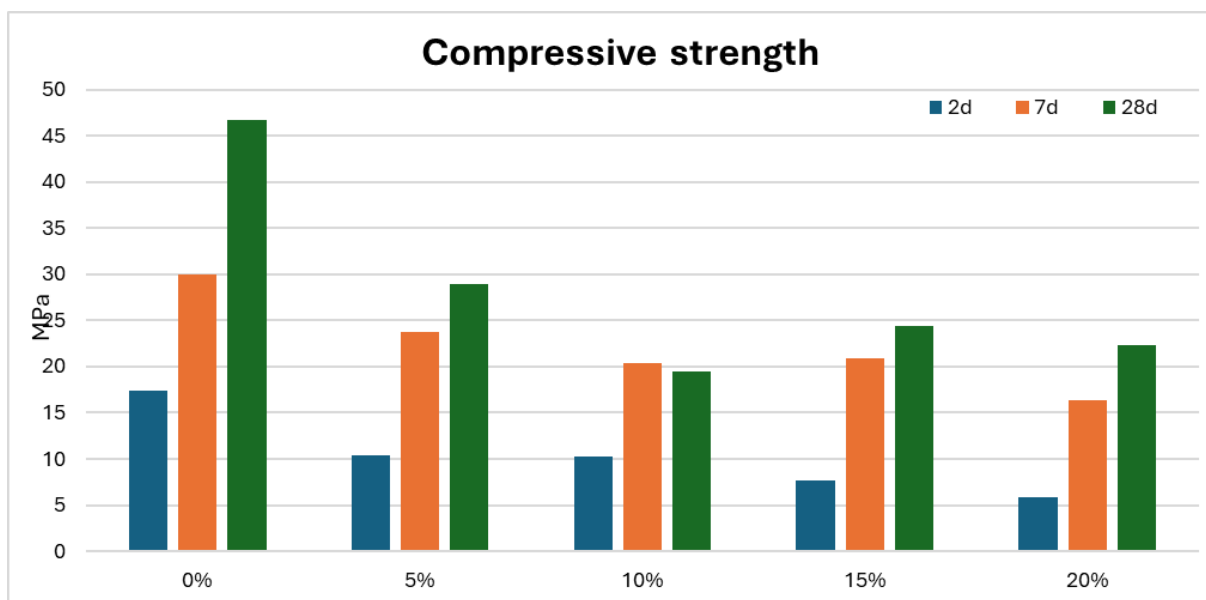


Figure 3.18. Mortar compressive strength with replacement of standard sand with different percentages of volcanic lapillus.

3.5.2 MICROSTRUCTURAL ANALYSIS

The microstructural analysis was performed on the samples containing 5% and 20% lapillus at 2 and 28 day curing in order to assess the degree of compaction and the possible formation of cementitious gel over time.

In *section 3.3.2*, the microstructure of the samples containing 5% and 20% lapillus as SCM of CEM II 42.5 was analyzed; in this case, in addition to analyzing the microstructure of the samples, a comparison with the previous formulations will be made.

In **Figure 3.19 (a-c)**, the microstructure of the sample containing 5% lapillus 2 and 28 days cured respectively can be observed. The microstructure, shown in **Figure 3.19 a**, appears very granular, with sporadic small needles (red circle) that could identify the formation of ettringite. The formation of a very granular gel would lead to thinking of a low reactivity of the raw materials during the maturation period under consideration. If the microstructure is compared with that of the sample containing 5% lapillus as SCM in CEM II 42.5 and cured for 2 days (**Figure 3.19 b**), it can be seen that the alternation between the sand and the granules forming the cementitious gel is more pronounced, while the ettringite takes on a more pronounced shape (red circle). The above is also reflected in the macrostructures, therefore at lower magnifications: comparing the structures in **Figure 3.19 (c-d)** it can be seen that surface *c* (standard sand replacement, 28 days of curing) is less homogenous and made up of microgranules unlike surface *d* (cement replacement, 28 days of curing) which is more homogenous. Both samples are characterized by the presence of small cracks on the surface which, however, should not affect the compressive strength of the material. The compressive strength of the material containing lapillus instead of standard sand could be lower as the presence of larger granules could lead to an increase in the porosity of the material, thus conferring preferential breaking channels. In **Figure 3.19 a** there would appear to be diffuse porosity and in greater quantity than in **Figure 3.19 b**. The problem of diffuse porosity developing between the gel of C-S-H is also due to aspects related to the durability of the material; in fact, greater porosity makes the material more permeable and therefore increases the penetrability of the cement system by external agents. In order to reduce the porosity, and thus increase both mechanical strength and durability, one could reduce the w/c ratio so as to create a more densified gel.

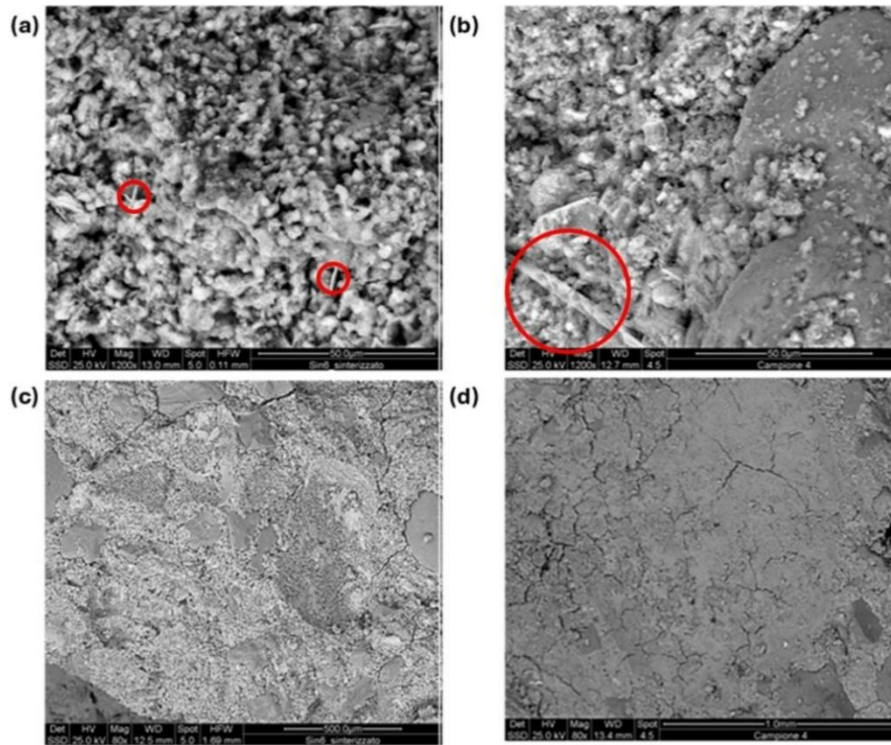


Figure 3.19. SEM images referred to: (a) and (c) sample with 5% lapillus instead of standard sand, (b) and (d) sample with 5% lapillus instead of clinker. (a) and (b) 2 days cured samples, (c) and (d) 28 days cured samples.

In **Figure 3.20 a** it can be seen that the above is confirmed, i.e. the presence of a more granular cementitious gel tends to form more porosity. The pore cavities turn out to be about 100 μm in diameter; when compared with the same composition, where lapillus is substituted for cement (**Figure 3.20 b**), the porosities turn out to be about 10 times larger than in sample *b*, which is about 10 μm in size. This greatly affects the mechanical properties of the material, resulting in a loss of compressive strength, as shown in *section 3.5.1*.

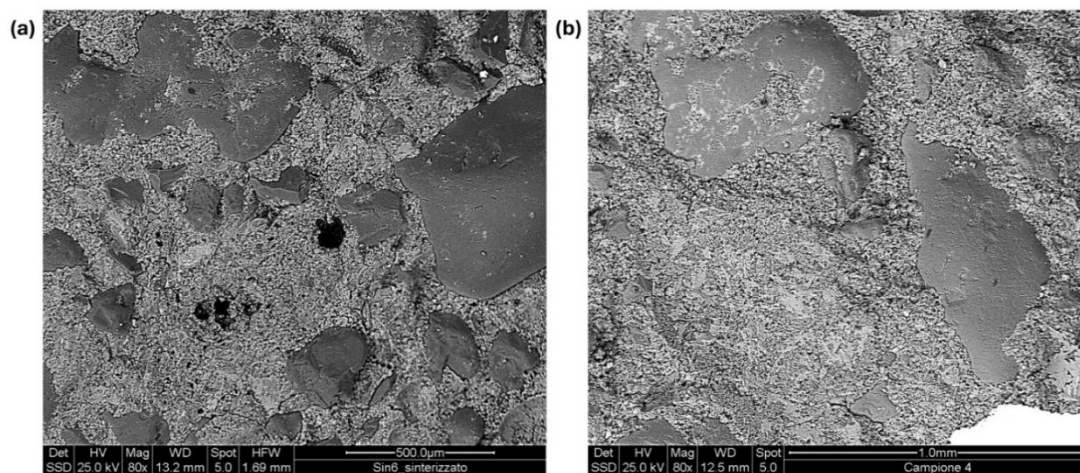


Figure 3.20. SEM analysis on 2-day cured samples containing 20% lapillus (a) in substitution of standard sand and (b) as SCM of cement.

3.6 CONCLUSIONS

In this chapter, the feasibility of using volcanic lapillus as a supplementary cementitious material (SCM) or aggregate in mortar production was evaluated.

In the first part, the partial replacement of Portland cement (CEM I 52,5 R and CEM II/B-LL 42.5) with volcanic lapillus scraps was evaluated in order to reduce environmental impact linked to the production of cement.

Key findings include:

- **Workability and Density.** Workability slightly decreased with higher lapillus content due to its porous nature, but the bulk density reduction suggests potential applications in lightweight construction.
- **Mechanical properties.** At short curing times, up to 10% replacement mortars showed a minimal reduction in compressive strength, while higher replacement levels (15-20%) led to a more noticeable decrease. At 90 days of curing however up to a 10% substitution, the compressive strength matches the one of the reference mortar.
- **Durability (CEM II/B-LL 42.5).** The presence of volcanic lapillus improved resistance to sulfate and alkali-silica reactions (ASR), reducing degradation risks.
- **Microstructural analysis (CEM II/B-LL 42.5).** SEM analysis confirmed good gel-aggregate adhesion.
- **Pozzolanic activity.** Thermogravimetric analysis (TGA) showed reduced calcium hydroxide content over time (CEM II/B-LL 42.5) confirming the pozzolanic activity.
- **Chloride penetration and Water Absorption.** While chloride diffusion increased slightly in higher replacement samples, capillary water absorption remained similar to the control at 10 % slightly increasing at higher lapillus content (CEM II/B-LL 42.5).

Overall, volcanic lapillus, despite its low amorphous fraction (around 16%) compared to others SCM, is interesting as an eco-friendly SCM, contributing to CO₂ emission reduction and durability improvements. However, further research is needed to optimize its use in high-replacement scenarios and address workability concerns.

In the second part, the partial replacement of standard sand with volcanic lapillus scraps was evaluated in order to use recycled aggregated and reduce the environmental impact linked to the use of virgin raw materials.

Key findings include:

- **Workability and Density.** Workability increased with higher lapillus content due to its porous nature. The true density measured after 28 days remained nearly constant, suggesting that long-term compaction is not significantly influenced by aggregate type.
- **Compressive strength.** Although compressive strength increased over time, the addition of lapillus significantly reduced mechanical resistance. Even small replacement levels (5%) showed notable strength losses.
- **Microstructural analysis.** SEM images confirmed that using lapillus as sand replacement results in a more porous and less homogeneous microstructure, with a granular cementitious gel and larger pore sizes compared to samples where lapillus is used as a cement substitute. This widespread porosity negatively affects both mechanical properties and material durability.

While the use of lapillus enhances mortar workability, it introduces drawbacks in terms of strength and durability due to increased porosity. To improve overall performance, it is advisable to reduce the water/cement ratio and explore strategies to control the water absorption and release characteristics of lapillus.

4. MICRONUTRIENT-CONTAINING FERTILIZERS ON ZEOLITIC TUFFS/PUMICE CARRIERS

4.1 STATE OF THE ART

Micronutrient-containing fertilizers play a crucial role in modern agriculture by supplying essential elements such as boron, cobalt, copper, iron, manganese, molybdenum and zinc, which are needed in small amounts but are essential for plant growth and development.

To provide fertilizers to the aerial part of plants, the use of microporous cation exchange materials could be a viable option [[224]-[229]]. Among these, zeolites are very promising geomaterials [230][231][232][233][234]. Indeed, zeolites are characterized by properties such as high and selective cation exchange capacity (CEC), reversible hydration, and molecular sieving, which give them high agronomic value [235][236][237]. This success is confirmed by numerous studies and applications concerning their use as soil conditioners [[238]-[251]], for nutrient recovery from wastewater and livestock manure [249][[252]-[258]], and, more recently, as corroborants for foliar treatments, due in part to their persistence on leaf surfaces when applied in micronized form [240][[259]-[269]].

Although recent studies show that zeolites synthesized from wastes such as fly ash and bottom ash can be used in a variety of application contexts [268][269][270], volcanic tuffs are currently used almost exclusively in agriculture [271]. Volcanic tuffs are rocks that can contain up to 70-80% by weight of zeolitic species, such as clinoptilolite, mordenite, phyllipsite and chabazite, in varying amounts depending on the genetic conditions and geological history of the area. It is important to note that the use of zeolitized tuffs in agriculture does not necessarily imply the opening of new quarries, but rather the exploitation of by-products of existing quarries. In the past (and to a large extent still today), zeolitized tuffs were used to obtain natural building stone; over the years, significant amounts of zeolite-rich waste have accumulated that can be profitably used in various large-scale applications [240][245][246][249], becoming a central business for many quarries.

On the other hand, there are more problematic quarry by-products, such as those resulting from the extraction and processing of pumice and lapillus, highly porous rocks of explosive volcanic origin. However, both pumice and lapillus, like tuffs, can contain non-negligible amounts of zeolitic species (up to 15% by weight), making these geomaterials potentially effective as cation exchangers. Unfortunately, according to the regulations currently in force in Italy [272], and

indirectly applied in other nations as well, only geomaterials containing at least 50% by weight of zeolitic species, regardless of whether they are by-products, can be classified and marketed as soil improvers, which is the main source of consumption of these by-products in agriculture. Therefore, finding alternative ways to use geomaterials with modest zeolitic content is a current challenge, with not only environmental, but also managerial and economic implications, considering that the mining sector is a major source of waste production, generating globally more than 100 billion tons of solid waste in the form of rock fragments each year [273].

In the face of numerous studies on the use of zeolites for the removal of zinc (Zn) in environmental applications, only very little research has considered them as efficient geomaterials for Zn fertilization of soil or plant leaves [274] or for modeling the mobility of heavy metals, including Zn, in zeolite-treated soils, with implications for their bioavailability as well [275][276]. Zn is a key micronutrient for humans, being responsible for catalytic, structural and regulatory functions in mammals [277]. About 33% of ingested Zn is actually absorbed in the small intestine, transported to the liver and finally to other tissues via the systemic circulation [278]. Cellular stores of Zn are regulated by influx or release from intracellular stores of Zn or supplied by metallothioneins (proteins that bind Zn and act as intracellular stores) or heavy metal ATPases (enzymes that control Zn in the cytosol using adenosine triphosphate energy) [279].

The importance of Zn to the human body is highlighted by the numerous roles of zinc-finger proteins (Zn-finger proteins), which control the expression of growth-related genes, immune response mediators, and steroid receptors [280]. Despite this, Zn deficiency is a growing threat, especially in poor and developing countries, causing increased susceptibility to infection, reduced physical strength, growth retardation, and neurobehavioral deficits in children [281][282][283][284]. The main causes of low dietary intake are low levels of bioavailable Zn in agricultural soils (about 50% show inadequate levels of Zn) and non-diversified grain-based diets [285][286][287].

Zn is also essential for plant health because it is a key component of Zn-binding proteins and has structural functions. It is involved in transcription, translation, photosynthesis, and metabolism of reactive oxygen species [288]. In addition, Zn is important for plant-pathogen and plant-parasite interactions [289]. Indeed, increased levels of Zn have been associated with enhanced immune response and resistance to pathogenic infections, while deficiencies correlate with increased susceptibility to fungal diseases [290][291].

For plants, radial transport of Zn to the xylem (and thus to the shoots) occurs through two main pathways: the symplastic and apoplastic pathways. In all cases, the presence of Zn in a bioavailable form is crucial. Stimulating Zn bioaccumulation in plants (biofortification) could be a solution in contexts where crop demand for Zn is not fully met by soil availability [[292]-[297]]. However, the effectiveness of Zn fertilization in soils is often limited by the high solubility and rapid leaching of Zn mineral fertilizers, cation exchange reactions with clay minerals and organic matter, and limited translocation from roots to edible parts of plants [[298]-[306]].

For these reasons, foliar application of Zn has gained popularity as an alternative or complementary strategy to soil fertilization [307][308]. Recent promising scientific studies [309][310][311] have demonstrated, by isotope tracing with Zn, efficient translocation of Zn from leaves to wheat grains, further confirming foliar fertilization as a preferred technique.

Based on these assumptions, a new gradual-release foliar fertilizer of Zn [312], composed of a mixture of zeolite-containing quarry by-products (clinoptilolite-rich zeolitized tuff, pumice, and lapillus waste), was sought, with the aim of reducing environmental impact and extraction costs. This formulation is expected to release Zn gradually over a longer period than conventional fertilizers, ensuring a constant supply of Zn to plants and minimizing losses through leaching. The possible presence of different zeolitic species in the various geomaterials used could offer advantages in terms of differential Zn release (i.e., kinetics), as each zeolitic species reacts differently depending on its crystalline chemistry [313][314][315][316].

Manganese (Mn) is also an essential micronutrient; it is involved in photosystem II for energy production in plants. It also serves as a cofactor in numerous enzymes, including hydrolases, oxidoreductases, and enzymes that catalyze phosphorylation and decarboxylation [317][318].

The bioavailability of Mn in soils depends mainly on soil pH. Mn can occur in different oxidation states, but the most bioavailable form is Mn^{2+} . However, less soluble forms, such as Mn^{3+} and Mn^{4+} , prevail in alkaline soils, thus reducing the availability of Mn for crops [319]. In case of deficiency, the most common symptoms are internerv chlorosis, manifested by yellowing of leaves with green veins, stunted growth and reduced development, as well as the appearance of necrotic spots [320][321][322]. On the other hand, excess manganese can be toxic to plants, interfering with the uptake of other essential nutrients and causing oxidative stress [[318]-[323]]. Some plants have developed tolerance mechanisms that include storing manganese in specific parts of the cell, such as the cell wall and vacuoles

(compartmentalization), to mitigate damage [324]. Numerous studies report the use of Mn-based fertilizers. Some of them have shown that cadmium (Cd) accumulation in rice crops is significantly reduced by the use of Mn-containing fertilizers combined with inorganic alkaline fertilizers and urea [325] or through fertilizer-induced manganese oxide formation [326]. In most cases, foliar application of fertilizers is preferable because it ensures greater uptake by the plant, as Mn bioavailability depends on soil pH. Understanding the interactions between adjuvants, agrochemicals and foliar fertilizers is crucial to improving the effectiveness of applications. One study examined the influence of manganese-based foliar fertilizers (manganese sulfate and manganese nitrate) mixed with an insecticide (chlorantraniliprole) and an organosilicone surfactant on solution rheological properties, cuticular penetration, and deposition characteristics on the cuticle of tomato fruits [327]. Another study evaluated the impact of foliar fertilization with zinc (ZnSO_4) and manganese (MnSO_4) on cesium (Cs) uptake by spring wheat and potato, showing that: (i) fertilization can increase crop yield, but its efficacy depends on climatic conditions; (ii) reduced Cs transfer is due to both nutrient addition and increased plant yield; (iii) zinc reduced Cs uptake in wheat, while manganese produced the opposite effect [328]. In addition, foliar uptake of manganese (Mn) and phosphorus (P) in nutrient-deficient spring barley was studied, observing that Mn uptake is promoted by a thin cuticle and increased stomatal density, with accumulation in epidermal cells and mesophyll, rapidly restoring photosynthetic processes [329]. Another study, conducted on two consecutive wheat growing seasons, evaluated the efficacy and cost-effectiveness of different Mn treatments to improve yield and Mn uptake by the plant [330].

In general, studies on agricultural products based on Mn and other micronutrients are increasing, highlighting their potential in improving agricultural production and food quality.

In the area of fertilization, zeolitized pumice and tuffs could be used for the gradual release of manganese (Mn^{2+}), since this when supplied to the soil tends to precipitate in insoluble forms, especially in alkaline soils, limiting its availability to plants. Delivery of Mn through zeolitized pumice and tuffs could ensure a more gradual and effective release, reducing the risk of toxicity or excessive leaching.

Only recently has the scientific community recognized the potential of pumice for water and wastewater treatment. In fact, natural or suitably modified pumice has been successfully used for the removal of heavy metals from aqueous solutions. The presence of small amounts of minerals belonging to the zeolite family has been linked to the reactivity of some pumice materials toward specific chemical species and their adsorptive properties. Zeolites are

aluminosilicates composed of structural tetrahedra $[\text{SiO}_4]^{4-}$ arranged in a three-dimensional microporous structure with interconnected channels and cavities [331][332]. Due to the partial substitution of Si^{4+} with Al^{3+} in the tetrahedra, the resulting $[\text{AlO}_4]^{5-}$ give the zeolites a net negative surface charge, weakly balanced by loosely bound cations. CEC is probably the best known and most exploited property of zeolites, as it allows cations present in aqueous solution to diffuse from the external environment to extra-structural spaces, while cations originally present on internal surfaces diffuse outward [235][333][334].

Zeolites are found in both hydrothermal and diagenetic environments, but economically exploitable deposits are mainly associated with diagenetic deposits [238][247]. Despite the possible presence of significant amounts of zeolites in pumiceous rocks subjected to diagenetic processes-sometimes up to 15% by weight [143][250][335][336]- these minerals are more commonly found in larger amounts, occasionally greater than 50% by weight, in diagenic volcano-sedimentary deposits, generally known as zeolitized tuffs [238].

The cation exchange capacity (CEC) of zeolitized tuffs depends not only on the amount and type of zeolites present (the main ones in diagenetic environments are chabasite, phyllipsite, clinoptilolite, and mordenite), but also on other properties such as grain size, porosity, and the presence of non-zeolitic phases. As a result, zeolitized tuffs find applications in various fields, including wastewater treatment, construction, gas adsorption, moisture and odor control, and agriculture [6][236][237][334][337]-[342]].

Agricultural applications are receiving increasing interest. Adding zeolitized tuffs to soil can increase water retention capacity, potentially counteracting drought stress and related plant damage [238][240]-[247][343]. In addition, zeolitized tuffs enriched with NH_4^+ -N recovered from livestock waste, and subsequently added to the soil, showed lower leaching than conventional organic and synthetic nitrogen fertilizers [239][242][243][248][249][251]. Nitrogen-enriched zeolites also temporarily altered soil pH, with a chalky effect that could promote nutrient mobilization [251].

Another application of natural zeolitized tuffs, when finely ground into powder, is their use as foliar coatings [240][259]-[263][265]-[267]. In the case of micronutrient deficiencies, for example, zeolitized tuffs can be enriched with micronutrients and sprayed on plant leaves, acting as a foliar corroborant with potentially superior resistance to rainfall runoff compared to conventional products [335]. In addition, foliar treatments with powdered zeolitized tuffs have

proven effective against insect pathogens, particularly the olive fly (*Bactrocera oleae*, Rossi 1790) in olive groves [234].

Due to the wide range of applications mentioned above, solid wastes from the extraction of zeolitized tuffs are generally negligible. However, as discussed above, this is not the case for pumice deposits, for which new areas of application need to be identified.

Accordingly, the potential of pumice waste for the removal of Mn^{2+} from aqueous solutions and its subsequent release for agricultural purposes was investigated. The activity of pumice wastes toward Mn^{2+} was compared with that of a better known and used zeolitized tuff. Manganese was chosen because it is an essential micronutrient for plants, and Mn^{2+} -enriched pumice, as well as Mn^{2+} -enriched zeolitized tuff, could prove effective for foliar applications. In fact, direct application of Mn to soil has disadvantages, as manganese tends to precipitate in insoluble forms, especially in alkaline soils, where the predominant cationic species are Mn^{3+} and Mn^{4+} [344]. Furthermore, when soluble Mn^{2+} , such as $\text{MnSO}_4\cdot\text{H}_2\text{O}$, is supplied through soil fertilization, its high availability may exceed the capacity of roots to absorb it or cause toxicity in plants, interfering with the uptake of other essential nutrients and causing oxidative stress [344][345]. Therefore, gradual release, potentially achievable with Mn-enriched zeolitized pumice and tuffs, could be a viable option to improve the effectiveness of Mn fertilization.

Positive results from this study could bring economic benefits to the mining industry and, more importantly, environmental benefits by turning a byproduct into a new resource for water treatment and agricultural application, with a potential phase release on plant leaves.

4.2 PART 1- ZN-BASED SYSTEMS: MATERIALS AND METHODS

4.2.1 RAW MATERIALS AND SAMPLES PREPARATION

The raw materials used were: clinoptilolite-based zeolized tuff (ZT), pumice rock (PU) and lapillus (LA), described in *Chapter 1*.

The absence of data in the literature on zeolite-based materials designed for controlled Zn release results in a lack of benchmarks for preparing different geomaterials and reagents. Therefore, it is necessary to take a benchmark independent of the material formulation and adapt the latter to the former. Considering that for foliar applications the recommended doses of Zn usually range between 200 and 300 g/ha, a formulation containing about 20 mg of

exchangeable Zn per g of geomaterial (equivalent to 61.2 mEq of Zn^{2+} per 100 g) would be suitable; in fact, it would mean using between 10 and 15 kg/ha of material (powder), an amount which parallels those usually required in most foliar applications with natural corroborants.

Four different formulations were prepared, identified hereafter as $\text{ZT}^{70}\text{PU}^{30}$, $\text{ZT}^{70}\text{LA}^{30}$, $\text{ZT}^{85}\text{PU}^{15}$ and $\text{ZT}^{85}\text{LA}^{15}$ composed of 70 or 85 wt% of ZT and 30 or 15 wt% of PU or LA, respectively. Preparation was done by simultaneously grinding appropriate amounts of each geomaterial in an agate mill until an impalpable powder was obtained.

4.2.2 METHODS

4.2.2.1 CHEMICAL, ELEMENTAL AND MINERALOGICAL ANALYSIS

Quantitative chemical analyses on solid were performed on powders using the Panalytical Zetium sequential wavelength dispersive spectrometer (WDS). Measurements are made on tablets obtained by pressing at 15 tons for 3 minutes 2.7 grams of sample mixed with 0.27 grams of organic resin on a support formed by boric acid.

Elemental analyses (carbon and nitrogen) were performed on a small amount of powdered material (about 3 mg) with a Carlo Erba model 1106 elemental analyzer (Carlo Erba Instrument, Milan, Italy).

Powder diffraction measurements were made at room temperature using a Philips X'Pert PRO diffractometer equipped with a first-generation Real Time Multiple Strip (RTMS) detector. NIST SRM 676a (alumina powder, corundum structure) was used as the internal standard for the quantitative analyses performed by the Rietveld method using the General Structure Analysis System (GSAS) software package and EXPGUI as the graphical user interface and following the protocol reported in Gualtieri et al. (2019) [346].

4.2.2.2 MICROSTRUCTURAL ANALYSIS

Microstructural analyses were performed by dispersing about 1 mg of powder on an aluminum stub previously coated with carbon-conductive adhesive tape. The carbon-coated elements were observed with the JEOL JSM-6010PLUS/LA InTouchScope scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) detector. SEM-EDX measurements

were performed in high vacuum with an accelerating voltage between 5 and 20 keV for both imaging and elemental analysis.

4.2.2.3 CATION EXCHANGE CAPACITY, Zn^+ ADSORPTION AND DESORPTION KINETICS

Chemical analysis of solutions was also performed, and cation exchange capacity (CEC), Zn^+ adsorption kinetics and desorption were determined.

The content of Ca, Mg, K, Na and Zn in aqueous solutions was measured by the ICP-OES technique (ICP analysis, PerkinElmer Optima 4200 DV) after appropriate calibration with certified standard solutions.

CEC were evaluated following the ammonium acetate (NH_4Ac) method (modified from Kloster et al. [347]) and ISO/DIS 22171, which consists in saturating the exchange sites with $(\text{NH}_4)^+-\text{N}$, and by measuring Na^+ , Mg^{2+} , K^+ and Ca^{2+} ions released. A borosilicate glass column was prepared with a stopcock at the bottom, directed to a flask and passing through a Gooch funnel with Whatman ashless filter paper. Some drops of NH_4Ac solution were used for wetting the paper and discarded. A mass of 1.5g of PU or LA was lad on top of the filter paper, where a total volume of 400 ml 1M NH_4Ac at pH 7 were dropped on top with a flow rate at about 1.5 ml/min. The leachate was collected in four distinct leaching volumes (100 ml each) and the amount of Na^+ , Mg^{2+} , K^+ , Ca^{2+} were determined by ICP-OES. For removing the residual NH_4Ac , the zeolitized tuff was washed directly in the funnel with 200 ml of Millipore water, slowly dropped on top. The material was then dried at 45 °C for 48 hours (low temperature was used to avoid ammonium thermal decomposition). The CEC was calculated from the sum of exchanged cations and – as a double check – by measuring the nitrogen content of the zeolitized tuff with an elemental analyzer.

To determine the adsorption of Zn^{2+} the optimal solid/liquid ratio was first defined. Different masses, ranging from 1.5 to 6g of finely grounded ZT were added to 50 ml of $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ 0.1M solution (previously acidified with a few drops of concentrated HNO_3 to facilitate solubilization) in closed PVF flasks and mixed at 400 rpm for 24 h at 20 °C. Suspensions were then centrifuged at 6000 rpm for 4 min and the supernatant was separated and immediately acidified with 65% HNO_3 (1:20). Samples were then stored at room temperature in closed PVF flasks until measurements. Zn in solution was measured by ICP–OES.

Once the optimal solid-liquid ratio was defined (using a ZT dosage of less than 6% w/v), Zn^{2+} adsorption kinetic and the kinetic of the principal cations exchanged were accessed. Masses of 3 g of ZT were added at 50 ml of $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ 0.1M solution (6%) in closed PVF flasks and mixed with an orbital shaker at 400 rpm. The solid and liquid fractions were then separated at different times (0.5, 1, 1.5, 2, 3.5, 7, 14 and 28 hours) by centrifugation at 6000 rpm for 5 minutes. Concentrated HNO_3 was added at 1:20 (v/v). The released Na^+ , Mg^{2+} , K^+ and Ca^{2+} were analysed in the liquids by ICP–OES and used for calculating the amount of adsorbed Zn^{2+} through cationic exchange reactions.

In order to evaluate batch desorption, solid mixtures were loaded with Zn^{2+} . Four batches were prepared, one for each formulation, in a 1:50 solid/liquid ratio and allowed to interact for 10 hours, an adequate time to have a sufficient amount of adsorbed metal based on adsorption kinetic experiments. An aliquot of material consisting exclusively of ZT was prepared in the same way. At the end each solid was separated from liquid, washed with Millipore water, dried at 45 °C and characterized for Zn content after nitric-hydrofluoric digestion.

For each Zn-loaded formulation and for pure ZT, five sealed tubes consisting of 300 mg of powder and 50 ml of pH 5 to 6 solution, obtained by adding a few drops of acetic acid to 1 L of Millipore water, were prepared. The tubes were then placed on an orbital shaker at 320 rpm and removed at predetermined times (0.5, 1, 2, 4 and 6 hours). Before separating the solid from the liquid by centrifugation at 6000 rpm, the pH was measured and no significant changes compared with initial value were observed. Once separated from the solid, 2 ml of HNO_3 was added to each solution and then characterized for Zn content by ICP-OES.

4.2.2.4 RESIDENCE TESTS ON VITIS VINIFERA LEAVES

Based on the results obtained, it was decided to perform a residence test on *Vitis vinifera* leaves. Fifteen plants were sprayed, 5 with the formulation ($\text{ZT}^{70}\text{PU}^{30}$), 5 with $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ solution (positive control) and 5 with water (control). The plants were grown in pots and had a height of about 180 cm at the time of treatments. Each plant received 3 treatments, each 48 hours apart, which provided, on average, a total of 20 mg Zn per plant (regardless of the source of the metal, i.e., $\text{ZT}^{70}\text{PU}^{30}$ or ZnSO_4). Twenty-four hours after the last treatment, 3 leaves were randomly collected from each plant; then a 6-mm rainfall (1.5 mm/h for 4 hours) was simulated (**Figure 4.1**). The test used tap water. Twenty-four hours later, 3 leaves per plant were randomly collected at about the same location as before.

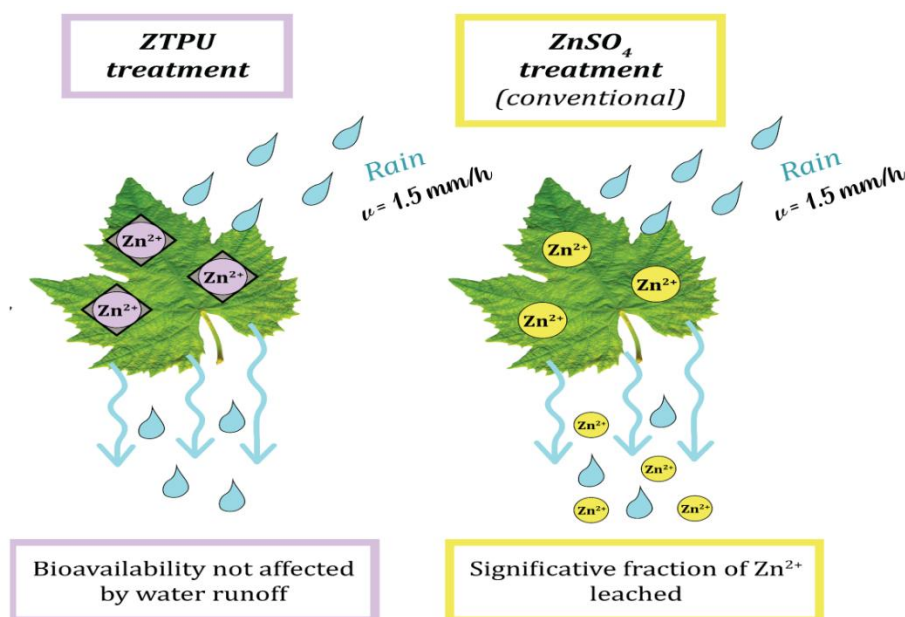


Figure 4.1. Sketch of the rainfall test performed, with tap water for 4 hours, on 3 randomly collected leaves after the last treatment.

Zn residence was evaluated by performing an extraction in water followed by an extraction in concentrated nitric acid [348][349]. For this purpose, 1.5 g of leaves dried in an oven at 120 °C for 48 h were shredded and placed in sealed containers with 30 ml of Millipore water and placed on orbital shaker for 24 h at 420 rpm. The water was then removed by filtering and acidified to 2% with nitric acid; after, 30 ml of HNO_3 65% was added to the solid residue and the containers placed back on orbital shaker at 420 rpm for 24 h. Again, the liquid was separated from the solid by filtration. A further check followed a more conventional procedure by analyzing total Zn in the ash obtained at 650°C and after digested in HNO_3 at 200°C. All the solutions were then characterized by ICP-OES for Zn content.

Data were subjected to statistical tests. To determine significant differences ($p < 0.05$), ANOVA and Tukey's HSD tests were performed in the case of normally distributed, homoscedastic populations (as resulted from Shapiro–Wilk and Bartlett's tests). Kruskal–Wallis was used for non–normally distributed, non–homoscedastic data. Statistical analysis was performed with R Studio (R Core Team, 2019), using MASS [350] and agricolae [351] packages.

4.3 ZN-BASED SYSTEMS: RESULTS AND DISCUSSION

4.3.1 MATERIALS CHARACTERIZATION

From a chemical and mineralogical point of view, it can be said that: ZT is characterized by a significantly high amount of clinoptilolite, with Na^+ , Ca^{2+} and Mg^{2+} as the main exchange cations, as suggested by CEC and chemical analyses (**Table 4.1**).

Chabazite and analcime are the zeolitic species found in PU and LA, respectively, but in lower amounts than in ZT, in accordance with the lower CEC of these two geomaterials, a parameter closely related to the amount of zeolitic species.

Hematite and pyroxene are also present in LA, in agreement with the higher Fe and Mg content in this sample compared to ZT and PU.

All samples are also characterized by a significant presence of undetectable material in X diffraction (likely amorphous), however, typical of geomaterials such as these originating from explosive volcanic events.

This feature is also well evidenced by the increase in background signal [237] that is observed for all samples between about 20 and 30 °2 θ (**Figure 4.2**); in fact, this increase is best evident in the PU sample, which is the one characterized by the greatest amount of amorphous.

Table 4.1. Mineralogical (weight %) and chemical (oxide weight %) composition of ZT, PU and LA. In the mineralogical analyses (left) the standard deviation σ_Q (values in parenthesis) of the weight percentage Q of each phase was calculated using the values obtained in the output file after the quantitative refinement by GSAS software, and the formula $\sigma_Q = \{[(\sigma_a/a)^2 + (\sigma_b/b)^2]^{1/2}\} Q$, where a and b are the two variables most affecting Q values and refer, respectively, to the weight fraction of the phase and the internal standard, whereas σ_a and σ_b are their standard deviations; "Amorphous" may also include very low-amount minor phases non detected through XRPD. In chemical analysis (right) the LOI (Loss On Ignition) is the weight loss (%) at 1050 °C. CEC are reported in mEq/100g as tCEC (theoretical CEC, cations exchange with $[\text{NH}_4]^+$ and aCEC (apparent CEC, cations exchange with Zn^{2+}). Counterions are referred to aCEC and were measured only for ZT being the main component of the formulations.

	ZT	PU	LA	ZT	PU	LA
Analcime	–	–	7.5(5)	LOI	12.7	4.30
Chabazite	–	12.4(2)	–	SiO ₂	64.2	60.5
Clinoptilolite	63.7(8)	–	–	Al ₂ O ₃	12.2	17.9
Hematite	–	–	7.8(3)	Fe ₂ O ₃	2.85	3.23
Mica/illite	2.7(2)	4.7(1)	1.8(6)	MnO	0.0821	0.143
Plagioclase	6.3(2)	3.9(2)	22.1(1)	MgO	1.47	0.946
Peroxene	–	–	14.6(9)	Na ₂ O	1.84	2.73
Quartz	2.0(5)	2.3(1)	0.80(7)	TiO ₂	0.298	0.393
Sanidine	2.9(3)	24.7(3)	7.6(6)	K ₂ O	1.87	7.55
Amorphous	22.4(9)	52.1(5)	37.8(8)	P ₂ O ₅	0.0611	0.0781
				CaO	2.38	2.42
χ^2	4.428	3.383	5.216	C	0.30	0.10
R_p	0.0550	0.0524	0.0924			
R_{wp}	0.0805	0.0738	0.0916	tCEC	159	22.3
				aCEC	83.4 of which:	
				Na ⁺	52.0	
				Ca ²⁺	15.3	
				K ⁺	4.55	
				Mg ²⁺	11.5	

The XRPD pattern of the geomaterials considered are reported in **Figure 4.2**. From a strictly qualitative point of view, XRPD results indicate that mica/illite, plagioclase, quartz and sanidine are present in all samples in varying amounts.

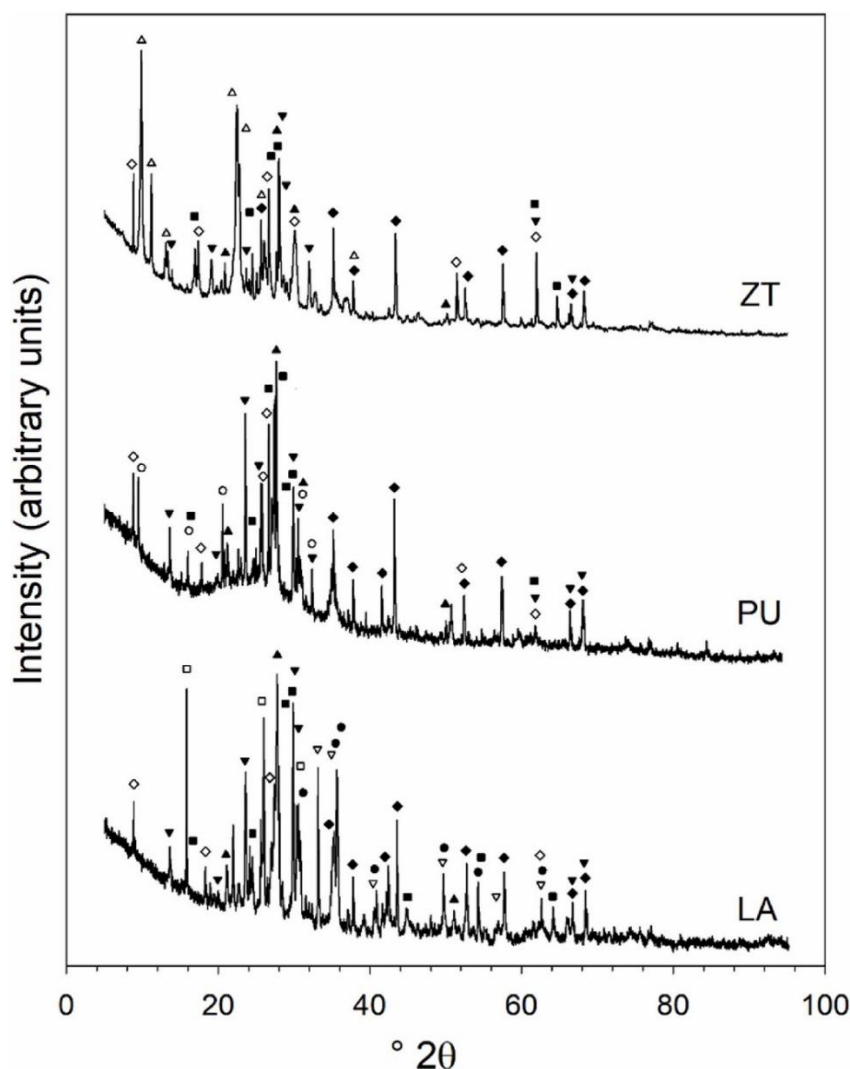


Figure 4.2. XRPD patterns of ZT, PU and LA. Symbols identify the main peaks of the detected phases (**Table 4.1**). Open symbols: square, analcime; circle, chabazite; triangle up, clinoptilolite; triangle down, hematite, diamond, mica/illite. Filled symbols: square, plagioclase; circle, pyroxene; triangle up, quartz; triangle down, sanidine, diamond, corundum (standard).

In agreement with its mineralogical composition (about 64 wt% of clinoptilolite) and as found for other similar geomaterials (clinoptilolite-rich tuffs) recently described in the literature [325][352][353][354][355] ZT has a specific surface area of $22.838 \pm 0.238 \text{ m}^2/\text{g}$. This value is close to that of PU ($18.005 \pm 0.099 \text{ m}^2/\text{g}$) and significantly higher than that of LA ($2.106 \pm 0.023 \text{ m}^2/\text{g}$). Although zeolitic tuffs generally have a slightly higher surface area than pumices due to their crystalline and microporous structure, a direct comparison between these

different materials is not possible because of the different geological context of origin and the different processing undergone [356].

4.3.2 Zn^{2+} ADSORPTION BY ZEOLITIC TUFF

The Zn^{2+} adsorption equilibrium test on ZT showed a peculiar Ce-qe curve, as Ce (Zn^{2+} in solution, mg/L) and qe (equilibrium adsorption capacity, mg/g) were negatively correlated (**Figure 4.2 A**). Inverse trends with respect to Ce are theoretically impossible in cation exchange, since they represent a condition where the higher the mass/volume ratio, the greater the exchange per unit mass. However, inverse correlations of qe with Ce can occur if some of the Zn^{2+} is released from the liquid phase and precipitates to form an imperfectly soluble salt. Indeed, the SEM-EDX analysis (**Figure 4.3**) carried out on the ZT powder obtained from the 6% p/v batch revealed the presence of domains with significant Zn% by weight, up to 70% by weight localized. As the ZT was washed several times with Milli-Q water after exchange, it must be excluded that these areas are formed by sulphate residues, as suggested by the absence of the sulfur signal in the EDS spectra (**Figure 4.3**). Considering that the total CEC of ZT was 159 mEq/100g, the maximum adsorption of Zn^{2+} cannot theoretically exceed 5.2 wt%. Although the EDX results are semi-quantitative, values significantly above 5.2 wt% cannot be fully explained by adsorption/exchange reactions but represent the possible presence of Zn precipitate (condition represented by red dots in **Figure 4.3 A** and **Figure 4.3 B**).

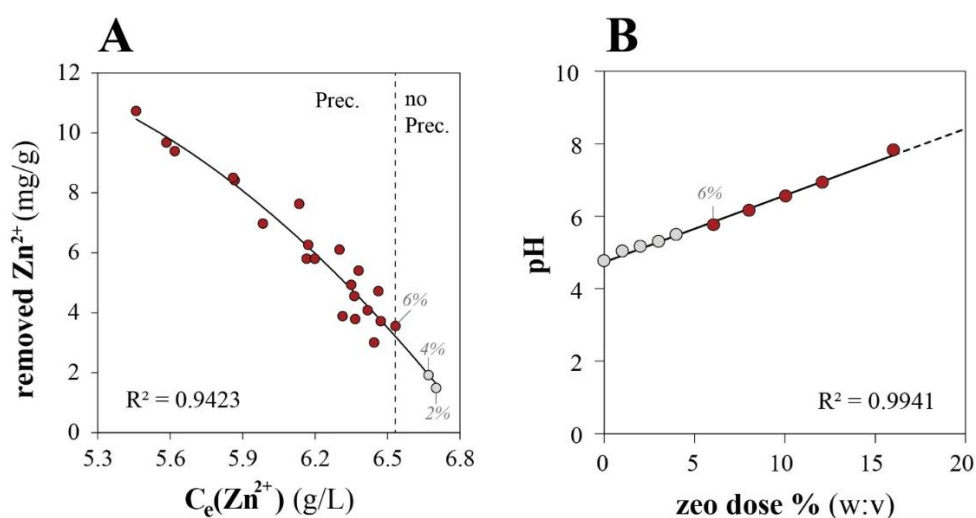


Figure 4.3. A) Removed Zn^{2+} at equilibrium per g of ZT, respect to residual Zn^{2+} dissolved. 2nd grade polynomial and R^2 are shown. The dotted vertical line separates the region where Zn precipitates occurred ($\text{ZT} \geq 6\%$ w/v, at the left) with the one

where no precipitates have been observed ($ZT < 6\%$ w/v, at the right); B) pH effect of different w/v ratios of ZT in $ZnSO_4 \cdot 6H_2O$ 0.1M solution. Percentages (%) are intended as w/v (g of ZT/100ml).

The precipitation of Zn phases was dose dependent ZT (**Figure 4.3 A**). The addition of zeolites to a solution can make significant differences in chemical properties, not only in terms of cation exchange, but also in terms of pH. More specifically, it has been shown that zeolites can significantly increase the pH of a solution [357] by promoting the precipitation of metal oxides and hydroxides [358]. The pH change was then tested from a solution of $ZnSO_4 \cdot 6H_2O$ 0.1 M in contact with different doses of ZT, with solid/liquid ratios ranging from 1 to 16% (w/v), in parallel. The samples were mixed at 400 rpm in sealed PVF bottles for 24 h when the pH was measured (**Figure 4.3 B**).

The initial pH was 4.8, slightly lower than the theoretical value (5.0) calculated with the following equation considering $pK_{a1} = 9.05$ and $C(s) = 0.1$ M [359]:

$$pH = 0.5pK_{a1} - 0.5\log(C_s)$$

The reason is due to the addition of small quantity of HNO_3 , used to facilitate the solubilization of $ZnSO_4 \cdot 6H_2O$. Once in contact with ZT, pH linearly increased with the ZT dose, to a maximum of 7.8 (reached at 16% w/v). The condition that first revealed Zn precipitates in SEM–EDS analysis (6% w/v) showed a pH of 5.8. It is therefore likely that pH changes by zeolitic minerals contributed to the precipitation of Zn phases, possibly represented by ZnO and $Zn(OH)_2$, as also suggested by McMahon et al. [360].

A grain of ZT material produced by the $ZnSO_4 \cdot 6H_2O$ treatment has been acquired in **Figure 4.4 A**. In the surroundings it is possible to notice smaller plate or tabular crystals. In **Figure 4.4 B** the areas outlined in red are those with Zn concentrations greater than 20% by weight.

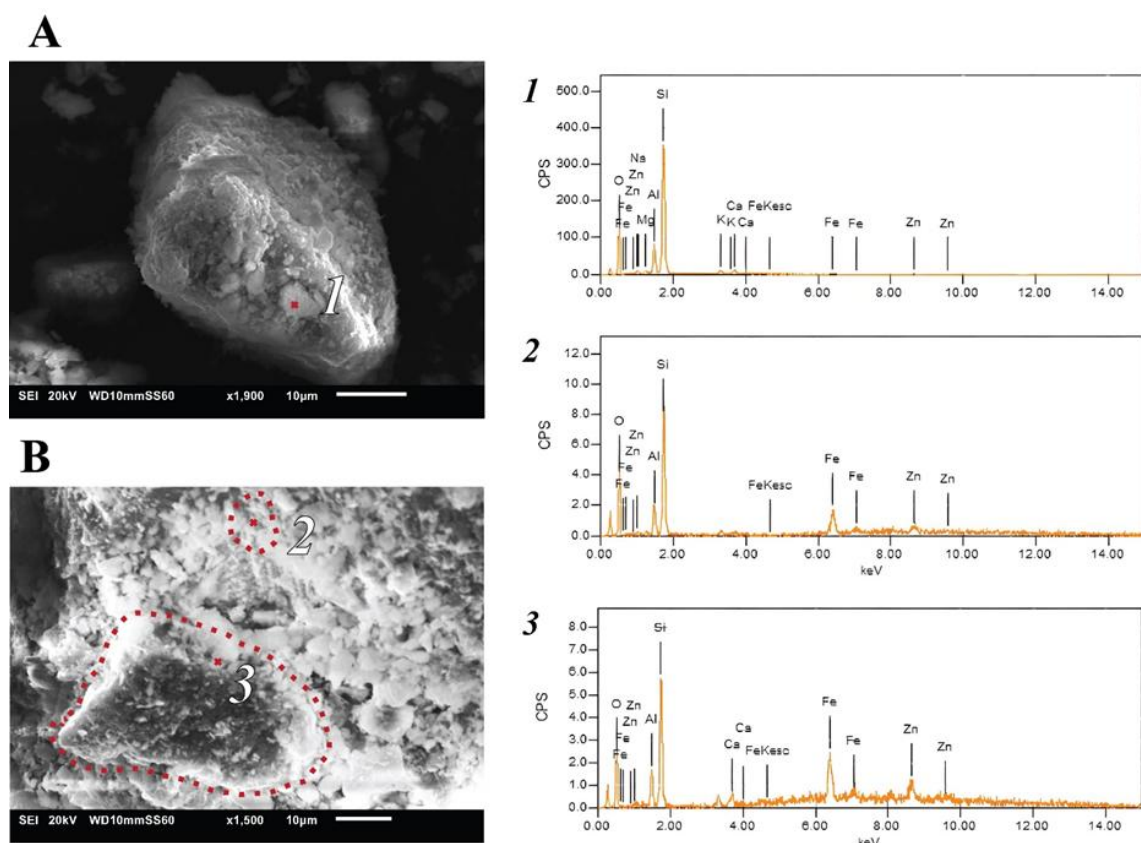


Figure 4.4. SEM–EDS of the ZT treated with $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ 0.1M solution (at 6% w/v batch). A) A grain surrounded by smaller tabular crystals; B) particular of a region with high Zn content (> 20 wt%), highlighted by red dotted lines. On the right the EDS spectra of measurements point 1, 2 and 3 indicated in Figs. A and B.

4.3.3 CATION EXCHANGE KINETIC OF ZT DURING Zn^{2+} ADSORPTION

Cations released were accessed in view of an industrial preparation process, therefore for their possible subsequent recovery. The results indicate that the equilibrium desorption capacities (q_e , measured at 28 h) for Na^+ , Ca^{2+} , K^+ and Mg^{2+} were 11.96, 3.07, 1.78, and 1.40 mg/g, respectively; corresponding to a total CEC of 83.4 mEq/100g (**Figure 4.5 A**). This total CEC is significantly lower than the one measured using NH_4^+ as the exchange cation (159 mEq/100g) because of the lower affinity of the zeolites towards Zn^{2+} compared to NH_4^+ [316]. However, with respect to ZT, it largely meets the target set (61.2 mEq/100g).

For each measured $q(t)$, the fractional uptake $F(t)$ was calculated as expressed by Simonin [361]: $F(t) = q(t)/q_e$, where $F(t)$ represents the closeness of the batch to equilibrium. As pointed out in Simonin [361], in kinetic investigation it should be avoided to use data too close to equilibrium, therefore it were considered only data with $F(t) < 0.85$. Distinct $F(t)$ values for exchangeable

cations are shown in **Figure 4.5 B**. The zeolitic tuff released monovalent ions (Na^+ and K^+) quicker than bivalent ones (Ca^{2+} and Mg^{2+}), reaching near equilibrium conditions ($F(t) \geq 0.85$) for Na^+ and K^+ after just 30 minutes of interaction, while Ca^{2+} and Mg^{2+} , where $F(t) \geq 0.85$, after about 4 hours. This difference in desorption kinetic between monovalent and bivalent cations can be explained by considering that, in general, cations with higher hydration energy – as Mg^{2+} and Ca^{2+} – present slower exchange kinetic than cations with lower hydration energy – as Na^+ and K^+ . Furthermore, zeolites with higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (as the ZT = 5.26) prefer monovalent cations [316][362].

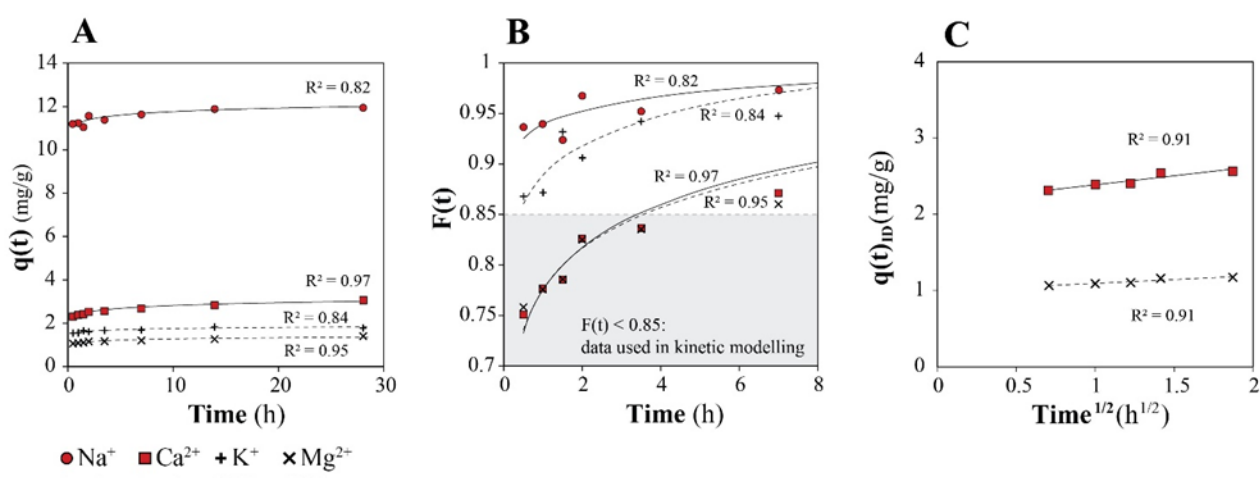


Figure 4.5. Desorption kinetic of Na^+ , Ca^{2+} , K^+ and Mg^{2+} by the zeolitic tuff in a $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ batch. A) $q(t)$ (mg/g) vs Time (h); B) $F(t)$ vs Time (h). The grey region represents $F(t) < 0.85$, therefore, the data contained were not considered in kinetic modelling. The curves in A and B are logarithmic regressions with R^2 indicated. C) Intraparticle Diffusion (ID) model for Ca^{2+} and Mg^{2+} and relative R^2 [363].

Only Ca^{2+} and Mg^{2+} provided data with $F(t) < 0.85$, therefore kinetic models were applied only for these cations. The Pseudo–Second Order (PSO), as firstly proposed by Ho and McKay [364], is showed in the following equation:

$$q(t) = \frac{q_e^2 kt}{1 + q_e kt}$$

where $q(t)$ (mg/g) is the adsorption/desorption capacity at time t , q_e (mg/g) is the adsorption/desorption capacity at equilibrium, k_2 is the PSO rate constant (g/mg h). The PSO showed a good correlation with experimental data ($R^2 > 0.999$), however not all the assumptions were plausibly met. These are highlighted in Xiao et al. [365], briefly: (i) adsorption is reaction–

controlled, (ii) liquid concentration is constant, and (iii) no desorption occurs. Indeed, to exclude spurious correlations, it has been pointed out to check the distribution of standardized residuals that in this case were not homogeneously distributed, finally confirming the inconsistency of the PSO model.

Being the ZT and, particularly, zeolite minerals porous materials, cations diffusivity could possibly be an important process in adsorption/desorption kinetic. Therefore, the classic Weber–Morris Intraparticle diffusion model (**Figure 4.5 C**) was applied, as illustrated in the equation:

$$q(t) = k_{ID}t^{0.5} + C$$

where K_{ID} is the diffusion rate constant and C (mg/g) is related with the diffusivity in the boundary layer, with higher values representing lesser limitations in diffusivity [366]. In the $q(t)$ vs $t^{1/2}$ plot, multi–linearity could be verified if adsorption occur via multiple phases, where the first step (line with intercept $C = 0$) represents external diffusion, followed by diffusivity–controlled adsorption [367]. Sole intraparticle diffusion occurs when a single line is present, intersecting the origin at $C = 0$, where K_{ID} is the slope.

The intercept C is also related to the thickness of the boundary layer (physisorption), where monolayer condition (chemisorption and cation exchange) is related with C values close to zero [366]. In this case, starting from 30 min of contact, C was 2.15 and 0.993 mg/g for Ca^{2+} and Mg^{2+} , respectively, while k_{ID} was 0.238 and 0.101 mg/g h. These values suggest that the diffusion of the exchanged species through the extra–framework spaces of zeolite toward the external environment did not significantly limit Zn^{2+} adsorption, at least starting from 30 min of contact.

The ZT was a finely micronized material, therefore the small particles increasingly exposed the pores to the external environment where the diffusion of cations outside and inside the zeolite minerals was plausibly facilitated. This aspect was likely particularly relevant for monovalent exchangeable cations, where the most present one (Na^{+}) showed an $F(t) = 0.94$ just after 30 minutes of contact, therefore suggesting no significative limitations in its diffusivity, while Zn^{2+} exchange occurred.

4.3.4 FORMULATIONS AND RELEASE OF Zn²⁺

As reported, four formulations were prepared by mixing different amounts of ZT with the by-products PU and LA, reducing the amount of ZT to a maximum of 30%, sufficient to ensure a CEC approximately equal to the fixed target. The four mixtures derived were ZT⁷⁰PU³⁰, ZT⁷⁰LA³⁰, ZT⁸⁵PU¹⁵ and ZT⁸⁵LA¹⁵ (numbers represent the relative wt% of ZT, PU and LA).

In **Table 4.2** it is possible to observe the total Zn adsorbed after exchange (mg/g) and the corresponding CEC (mEq/100g).

Table 4.2 Zn adsorption and CEC of the mixtures ZT⁷⁰PU³⁰, ZT⁷⁰LA³⁰, ZT⁸⁵PU¹⁵ and ZT⁸⁵LA¹⁵ (numbers represent the relative wt% of ZT, PU and LA) and ZT.

Formulation	Zn adsorbed (mg/g)	CEC (mEq/100 g)
ZT ⁷⁰ PU ³⁰	19.86	60.8
ZT ⁷⁰ LA ³⁰	20.16	61.7
ZT ⁸⁵ PU ¹⁵	23.00	70.4
ZT ⁸⁵ LA ¹⁵	22.7	69.4
ZT	26.71	81.7

The minor increase of Zn content in the formulations compared to the theoretical values that could be calculated from Zn-exchanged ZT (namely, –30% → 58.4 mEq/100g, and –15% → 69.5 mEq/100g) is consistent with the contribution to cation exchange of zeolitic species in LA and, especially, PU. Likewise, the amount of Zn in pure ZT is fully consistent with kinetic studies (slightly lower due to the shorter exchange time of 8 hours instead of 29). In fact, after 8 hours the equilibrium was almost reached (**Figure 4.5 A**) and this time saving, in front of only a minor decrease of CEC, is a key aspect for scale up.

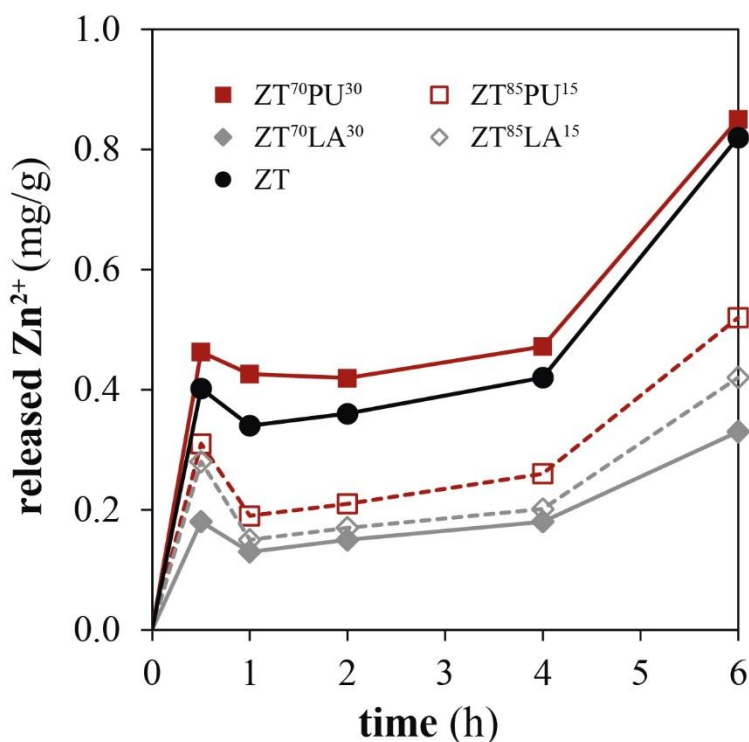


Figure 4.6. Release kinetic of the formulation ZT⁷⁰PU³⁰, ZT⁷⁰LA³⁰, ZT⁸⁵PU¹⁵ and ZT⁸⁵LA¹⁵ compared to pure ZT.

Release kinetic tests (**Figure 4.6**) show that for all the formulations the amounts of Zn²⁺ released after a contact time of 6 h were small (4.28, 1.63, 2.26, 1.85 and 3.07% of the total Zn present in ZT⁷⁰PU³⁰, ZT⁷⁰LA³⁰, ZT⁸⁵PU¹⁵, ZT⁸⁵LA¹⁵ and pure ZT, respectively), indicating that the Zn²⁺ retained by the formulations could be gradually released. The initial peak release (30 min) is due to the increased ease of exchange with cations located in the outermost part of the zeolitic channels, also facilitated by the reduced grain size. This peak is more pronounced (higher release) in the ZT⁷⁰PU³⁰ formulation, even compared to the pure ZT, reflecting the presence of a non-negligible amount of chabazite in PU, which has a higher CEC than clinoptilolite [238][332] and thus speeding up the initial stage of the exchange process. In fact, at higher times the release curves of ZT⁷⁰PU³⁰ and ZT tend to converge, resulting from the higher occurrence of zeolite (and exchangeable Zn²⁺) in ZT than ZT⁷⁰PU³⁰. Similar considerations apply also to ZT⁸⁵PU¹⁵ and ZT⁸⁵LA¹⁵, although the difference is less pronounced due to the higher amount of zeolite (clinoptilolite) compared to ZT⁷⁰PU³⁰. The formulation ZT⁷⁰LA³⁰ shows slower kinetics and lower release due to lower zeolite content. In the window of 30–60 min, the Zn²⁺ slightly dropped, indicating possible re-adsorption of Zn²⁺ and/or precipitation, however, Zn²⁺ continue to be slowly desorbed over time.

4.3.5 RESIDENCE OF ZT⁷⁰PU³⁰ FORMULATION ON PLANT LEAVES FOLLOWING RAIN EVENT

ZT⁷⁰PU³⁰ was considered the best formulation among the four tested; therefore, it was used in plant leaves residence tests, in comparison with conventional ZnSO₄·6H₂O fertilizer. The water-soluble fraction of Zn and total Zn in leaves were determined before and after a controlled rainfall event.

Before the rain events, the leaves treated with ZT⁷⁰PU³⁰ and ZnSO₄·6H₂O showed no differences (PRE rain columns in **Figure 4.7 A**), being that same amounts of Zn were used; conversely, significative higher amount of soluble Zn²⁺ was recorded in ZnSO₄·6H₂O treatment respect to ZT⁷⁰PU³⁰ (**Figure 4.7 B**), that is possibly indicative of faster availability to the plant. However, ZT⁷⁰PU³⁰ showed significative better tolerance to the rain event, as highlighted by more pronounced Zn residency (both total and soluble forms) compared to ZnSO₄·6H₂O. This positive effect is plausibly due to the role of ZT and PU active particles, namely zeolite species, in enhancing the permanence of Zn²⁺ on leaves compared to the greater mobile ZnSO₄·6H₂O, therefore enabling better permanence after a rain event. The increased persistence is also correlated to the physical interaction between lithoid particles of the formulation and the rough morphology of the leaf surface, which facilitates its adhesion, a feature also highlighted by Rotondi et al. [367], in plant treated with a natural zeolitic tuff. In other word, ZT⁷⁰PU³⁰ not only acts as a carrier for Zn²⁺, but also as a support for its residence on leaves.

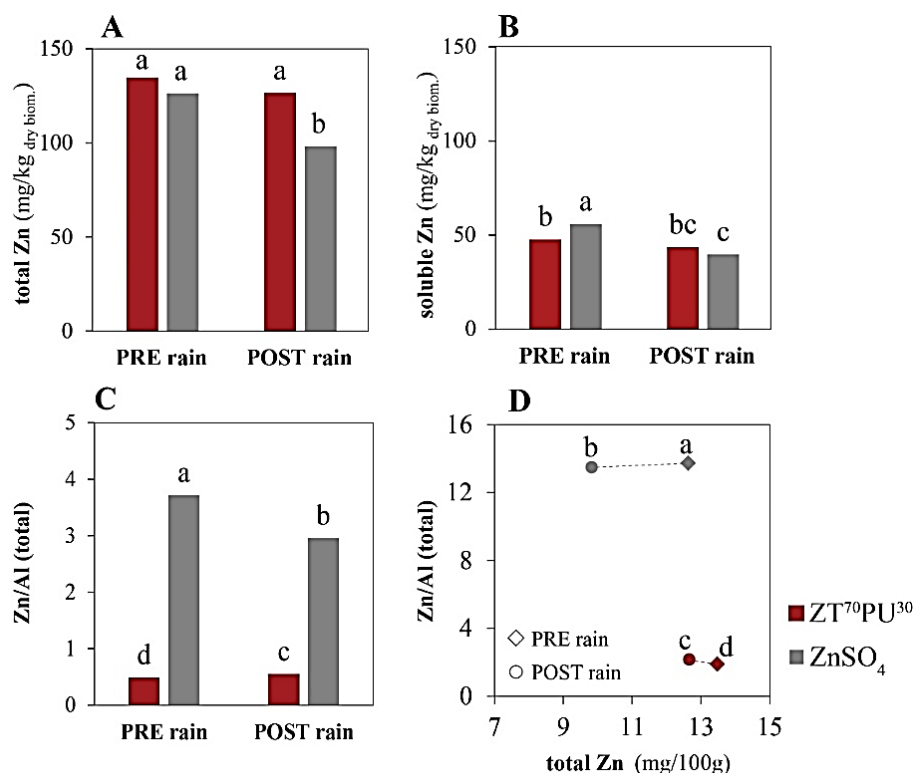


Figure 4.7. Zn concentration on leaves and residence time before and after a simulated rain event (PRE rain and POST rain, respectively), by ZT⁷⁰PU³⁰ and ZnSO₄·6H₂O treatments. A) total Zn (mg/kg dry biomass); B) soluble Zn; C) Zn/Al ratio; D) total Zn vs Zn/Al plot. Two conditions are significantly different if no letter (i.e., a, b, c, d) is in common, as resulted from ANOVA and Tukey's HSD tests.

The persistence of alumino–silicate minerals on the leaves is also proven by the total Zn/Al ratio (**Figure 4.7 C**) and by the comparison with total Zn (**Figure 4.7 D**). Lower Zn/Al ratios were recorded in leaves treated with ZT⁷⁰PU³⁰; however, it is relevant that the Zn/Al ratio decreases in ZnSO₄·6H₂O treated leaves after rain, compared with a small but noticeable increase in ZT⁷⁰PU³⁰, suggesting that the rain event does not significantly affect the persistence of mineral particles on leaves.

4.3.6 COST-BENEFIT ANALYSIS

Pumice and lapillus used in formulations and resulting from their extraction and processing operations have an average grain size of less than 3mm. This size severely limits their marketing since the main market is nursery gardening sector. However, we are talking about raw materials that turn out to be scraps and have very high operating costs, up to 2.50 €/m³. The scraps can be reused for quarry restoration with an additional cost due to transport from the plant to the quarry, or they can be stockpiled in areas within the quarry's jurisdiction that are authorized as

internal dumps and if resold a regional fee must be paid. It should be noted that these raw materials are extracted for other purposes, so reusing them would also have an additional benefit, which is environmental: one would not have the impacts associated with the extraction of virgin raw materials.

In order to obtain the product, it is necessary to consider the costs associated with the raw materials and energy required for its production, which are:

- Zinc sulphate: about 4 € per kg;
- Zeolitized tuff: about 0.15 € for a particle size of 0-6 mm and about 1.65 € per kg if the diameter is less than 20 µm;
- Pumice: about 0.015 € for 0-6 mm particle size and about 0.75 € per kg if the diameter is less than 20 µm;
- Lapillus: about 0.035 € for 0-6 mm particle size and about 0.55 € per kg if the diameter is less than 45 µm;
- Formulation energy consumption: about 6-7 €/kg.

Considering only the geomaterial, savings of 16.4% to 27% or 20% to 23%, depending on the average particle size, could be achieved by including 30% pumice or lapillus in the formulation. If the starting geomaterial is already micronized, production costs could also be reduced.

4.4 PART 2- MN-BASED SYSTEMS: MATERIALS AND METHODS

4.4.1 MATERIALS CHARACTERIZATION

The raw materials used were: chabazite-rich zeolitized tuff (CHA) and pumice (PUM), described in *Chapter 1*. Mineralogical and chemical compositions were determined as described in *Section 4.2.2*. The samples are electrically fused and obtained with an xrFuse (Xrf Scientific).

CHA and PUM were enriched in Mn^{2+} . The degree of Mn^{2+} enrichment in CHA and PUM was tested in a batch of 0.5 $\text{MnSO}_4\text{-H}_2\text{O}$ solution, at 6% dosage (m:v, namely 12 g in 200 mL). Samples were stirred in closed polypropylene tubes for 24 h at 400 rpm. The supernatant was then removed by centrifugation at 6000 rpm for 5 minutes. Powders were washed 5 times with 100 mL of Milli-Q water to remove weakly -bound and residual Mn^{2+} , then dried at 105 °C for 24 h, and calcined at 1050°C for 3 h. The total amount of Mn was measured by XRF technique

as for the virgin samples. The Mn^{2+} enrichment was calculated by comparing the total amount of Mn occurring in the Mn^{2+} -enriched samples versus the Mn in virgin samples. Localized clusters of Mn in the materials would indicate either the presence of residual Mn from the washings, or the occurrence of insoluble Mn-precipitates. Both these scenarios were not desirable. Therefore, to ensure that no Mn precipitates occurred during the adsorption batch, Mn-chemical mappings were performed with SEM-EDX technique (JSM-6010PLUS/LA, JEOL).

The t.CEC was accessed with the ammonium acetate (NH_4Ac) method, described in *section 4.2.2*. The exchange sites were saturated with a high-affinity cation (NH_4^+), and the displaced positive charges of exchanged cations (Na^+ , Mg^{2+} , K^+ and Ca^{2+}) were then quantified in the solution with ICP-OES technique.

The oxidation state of Mn is pH dependent. In acidic and neutral aqueous solutions, the most stable form is Mn^{2+} . Mn solubility strongly decreases in oxidizing systems with neutral or alkaline pH (Hem, 1972), where it easily precipitates as oxide and hydroxides by reacting with the dissolved oxygen and $(\text{OH})^-$. To be sure that the effects of adding CHA and PUM to the solution would be negligible on pH and thus on the possible precipitation of insoluble species, a 6% dose (m:v) of CHA or PUM (12 g in 200 mL) was mixed with a magnetic stirrer, in contact with a 0.5 M $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ solution, and the pH was monitored at 1, 30, 150 and 240 minutes of contact, with an Orion 9102BNWP pH-meter (Thermo Fisher Scientific, Waltham).

4.4.2 ADSORPTION KINETIC, ISOTHERMS AND Mn^{2+} RELEASE

In the adsorption kinetic tests, a 15% (m:v) dose of CHA and PUM was used. 6 g of each material was added to 40 mL of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ solution containing 1000 ppm Mn^{2+} . Samples were closed in polypropylene tubes and mixed with an orbital shaker at 400 rpm. The supernatant was then separated from the solution at 5, 10, 15, 30, 45, 60, 100, 130 minutes, and 14 h, which was assumed as close to the equilibrium.

Adsorption isotherms were investigated using the same batch volume (40 mL) and mixing rate (400 rpm) as in the kinetic tests, but with different masses of CHA and PUM: 1, 2, 3, 4, 5, 6, 7, 9, 11, 13 and 15 g. Equilibrium was assumed to be reached after 24 h of contact, at which samples were collected.

The kinetics of Mn^{2+} release from the Mn^{2+} -enriched CHA and PUM were evaluated. To simulate agricultural applications (foliar film technology), synthetic groundwater was used, designed to mimic the properties of water used with spraying machines. Therefore, to prepare the synthetic groundwater, the following reagents were used: 150 mg/L of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 150 mg/L of NaCl , 250 mg/L of NaHCO_3 , 500 mg/L of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 13 mg/L of KNO_3 , 65 mg/L of MgCl_2 and 100 mg/L of CaCl_2 . The resulting concentrations of dissolved ions were consistent with the composition of real non-saline groundwaters [368][369][370][371], namely (mg/L in parentheses): Ca^{2+} (71), Mg^{2+} (43), Na^+ (127), K^+ (5), SO_4^{2-} (224), Cl^- (178), HCO_3^- (182), NO_3^- (8).

CHA and PUM used in the desorption tests were previously enriched in Mn^{2+} as described below. A 13% dosage (m:v) was added to a $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ solution containing 1000 ppm of Mn^{2+} and mixed at 400 rpm with an orbital shaker for 180 minutes, which, according to the results of the kinetic tests, was sufficient to reach near equilibrium. Afterward, CHA and PUM were allowed to decant for 24 h and then separated using a vacuum filtration system consisting of a Buchner funnel with Whatman filter paper on top. Suction was provided by a water-jet vacuum pump connected to a tailed flask as a receiver. CHA and PUM were then washed twice by mixing approximately 200 g (dry weight) of each with 2 L of Milli-Q water, stirred with a magnetic stirrer for 30 minutes and separated using the same vacuum filtration system. The effectiveness of the washes in removing the reagent remained in solution ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) was evaluated by comparing the sulfur content in virgin versus treated samples through XRF measurements, which showed negligible differences.

Desorption kinetics were investigated by preparing polypropylene tubes containing 3 g of Mn^{2+} -enriched CHA or PUM and 50 mL of simulated groundwater (6% dosage, m:v). The samples were mixed at 400 rpm with an orbital shaker, and aliquots were collected at various time intervals: 15, 30, 60, 120, 180, 240, 360 minutes; 1, 2, and 5 days. For all the tests described in this section, dissolved 250 Mn^{2+} was measured in liquid samples collected and separated from CHA and PUM through filtration with Whatman ashless filter paper, followed by filtration with nylon syringe filters (0.2 μm in diameter). Each sample consisted of 10 mL of simulated groundwater, acidified with 100 μL of 65% HNO_3 . The concentration of dissolved Mn^{2+} was measured by ICP-OES. Modelling was carried out using R Studio (R Core Team, 2019), with isotherm and kinetic modelling performed using the PUPAIM [370] and PUPAK [371] packages, respectively.

4.5 MN-BASED SYSTEMS: RESULTS AND DISCUSSION

4.5.1 EFFICIENCY OF MATERIALS IN Mn^{2+} ENRICHMENT

Compared to CHA, the t.CEC of PUM was approximately one order of magnitude lower (0.173 vs. 1.487 mmol(+)/g) (**Table 4.3**). However, PUM showed a higher affinity for Mn^{2+} compared to CHA, as indicated by the percentage of saturation (Mn^{2+} sat.), which represents the percentage of the t.CEC (charge density) that can be occupied by Mn^{2+} charges (**Table 4.3**). As described, this parameter was derived by saturating the materials with 0.5 M $\text{MnSO}_4\text{H}_2\text{O}$. While the Mn^{2+} saturation in CHA was approximately 18% (i.e. 18% of the exchangeable charges were represented by Mn^{2+}), it reached 65% for PUM. Thus, despite its lower CEC, PUM had almost four times the affinity for Mn^{2+} than CHA.

Table 4.3. Amount (mmol(+)/g) of exchangeable (exch.) cations by CHA and PUM. The t.CEC is the theoretical cation exchange capacity, equal to the sum of the overall exchangeable positive charges of the counterions per g of material (mmol(+)/g). Mn^{2+} -EC is the enrichment capacity of the materials under saturation with 0.5 M $\text{MnSO}_4\text{H}_2\text{O}$. Mn^{2+} sat. represent the percentage (%) of the t.CEC available for Mn^{2+} enrichment, namely the maximum enrichment in Mn^{2+} achievable by the materials under the experimental conditions.

	exch. Na^+	exch. Mg^{2+}	exch. K^+	exch. Ca^{2+}	t.CEC	Mn^{2+} -EC	Mn^{2+} sat
	mmol(+)/g						%
CHA	0.037	0.070	0.402	0.977	1.487	0.273	18.4
PUM	0.001	0.022	0.061	0.089	0.173	0.113	65.2

The active mineral present in PUM is analcime, belonging to the zeolite family, and is present at 0.80 wt% (**Table 4.4**). Considering that the CEC of analcime is approximately 4.5 mmol(+)/g [332], the expected CEC contribution from analcime alone would be about 0.036 mmol(+)/g, which is significantly lower than the measured t.CEC (approximately 0.17 mmol(+)/g). Therefore, it is plausible that the detectable zeolites in pumice contributed minimally to the overall activity regarding Mn^{2+} and CEC, suggesting that active sites for Mn^{2+} may have been present in other phases of PUM, likely including the amorphous fraction, of the material, which constituted the majority of PUM (**Table 4.4**).

Table 4.4. Mineralogical and chemical composition of CHA and PUM. In the mineralogical analysis: i) the standard deviation is the values in parenthesis; ii) “other” identifies phases that are either undetectable because too small in quantity, or non-crystalline phases. In the chemical analyses LOI refer to the Loss On Ignition, namely the weight loss (%) at 1050°C.

Mineralogical composition (wt%)			Chemical composition (wt%)		
	CHA	PUM		CHA	PUM
analcime	-	0.80 (6)	LOI	10.1	6.01
chabazite	46.8 (5)	-	SiO ₂	53.8	56.2
sanidine	21.4 (3)	4.8 (2)	Al ₂ O ₃	18.2	19.5
orthoclase	-	2.4 (1)	Fe ₂ O ₃	3.66	3.87
phlogopite	2.5 (1)	-	MnO	0.10	0.14
muscovite	-	4.5 (1)	MgO	1.68	0.69
other	29.3 (5)	87.5 (2)	Na ₂ O	0.68	2.46
			TiO ₂	0.53	0.57
χ^2	16.40	1.526	K ₂ O	5.63	7.63
R_{wp}	0.0615	0.0447	P ₂ O ₅	0.12	0.11
R_p	0.0432	0.0349	CaO	5.23	2.53

Regarding the effect on the pH of the MnSO₄·H₂O solution, CHA and PUM increased the pH from the initial value of 5.73, to 6.25 and 6.30, respectively, after 240 minutes of contact. This increase was likely due to the release of alkaline counterions such as Na⁺, Mg²⁺, K⁺ and Ca²⁺. At room temperature, Mn²⁺ is coordinated by 6 water molecules, and the initial pH of 5.73 in a 0.5 M MnSO₄·H₂O solution results from the speciation of dissolved Mn²⁺ into two singly charged cations through hydrolysis of water in the hydration shell [372]: Mn²⁺(H₂O)₆ → MnOH+(H₂O)₅ + H⁺ where Mn²⁺(H₂O)₆ is the hydration shell in octahedral coordination. At 240 minutes of contact, equilibrium for pH was not yet reached; however, between 180 and 240 minutes, the increase was less than 1%, suggesting that a condition close to equilibrium was achieved. Nevertheless, the pH was always lower than 7, with the highest value measured in PUM at 240 minutes (6.30), therefore no Mn-precipitates were expected. To validate this hypothesis, semiquantitative chemical analyses were conducted using SEM-EDS technique on the Mn²⁺-enriched materials. No Mn clusters were observed in the materials, except for a few small, localized areas in CHA (**Figure 4.8 A-B**) that were also associated with Ti and/or Fe (**Figure 4.8 C-D**). The simultaneous presence of Ti and Fe indicates that these phases were already present in the original sample, and the flat morphology of the observable fragment in the lower right part of **Figure 4.8 A** suggests that it is a phlogopite crystal, in agreement with mineralogical analyses (**Table 4.4**). However, it cannot be ruled out that clusters with this chemical composition are also present in the amorphous fraction without however affecting the results obtained.

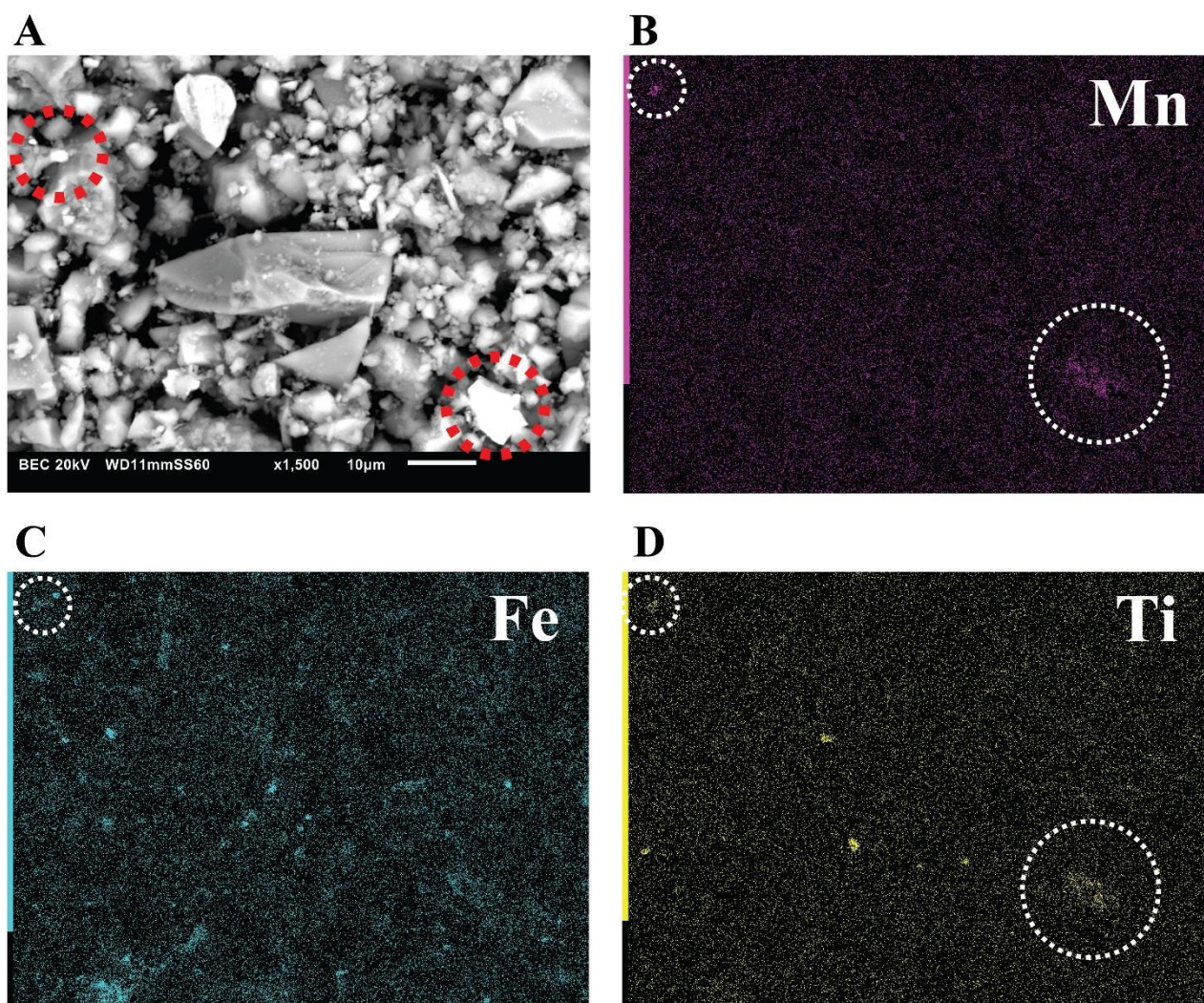


Figure 4.8. SEM-EDS imaging of the Mn^{2+} -enriched chabazite zeolitized tuff (CHA). A) Backscattered electron scanning of CHA, and map distribution of Mn (B), Fe (C) and Ti (D). Dotted lines mark localized regions with slightly greater concentration of Mn, in association with Ti and/or Fe.

4.5.2 KINETIC OF Mn^{2+} ENRICHMENT

Once it was assured that Mn-precipitates were absent, the enrichment of Mn^{2+} was investigated by CHA and PUM through kinetic and equilibrium tests. For kinetic investigations, it is advisable to avoid linearized models, as they can often induce statistical biases [373]. Additionally, data points close to equilibrium (e.g., when $q_t \approx q_e$) should be avoided as well. This is particularly relevant in the context of the frequent misuse of the Pseudo-Second-Order (PSO) model compared to the Pseudo-First-Order (PFO), as highlighted by Simonin [361]. Therefore, kinetic modelling was calculated using only data with a fractional uptake $F(t)$, defined as $F(t) = q_t/q_e$, that was equal to or less than 0.95.

Table 4.5. Statistical parameters of kinetic models and constants respect to Mn^{2+} -adsorption from $MnSO_4 \cdot H_2O$ solution for CHA and PUM. Avrami, Elovich, Fractional Power, Pseudo-First Order, and Pseudo-Second Order are non-linear models, while Weber-Morris Intraparticle Diffusion is linear. The acronyms of statistical parameters are: RMSE (Root Mean Square Errors), MAE (Mean Absolute Error), AIC (Akaike Information Criterion), SE (Standard Error) and the coefficient of determination (R^2), which is indicated only in the Weber-Morris intraparticle diffusion, representing the overall coefficient of determination of two distinct lines.

	Models	Statistics					Kinetic constants							
		RMSE	MAE	AIC	SE	R^2	param. 1	param. 2	param. 3	param. 4	param. 5	param. 6	param. 7	param. 8
CHA	Avrami	0.092	0.072	-15.2	0.102	-	k_{AV}	0.767	n	0.229	-	-	-	-
	Elovich	0.089	0.070	-16.1	0.098	-	α	$1.23 \cdot 10^3$	β	4.64	-	-	-	-
	Fractional Power	0.091	0.072	-15.6	0.100	-	α	0.610	β	0.080	-	-	-	-
	PFO	0.428	0.375	16.5	0.473	-	k_{PFO}	0.151	-	-	-	-	-	-
	PSO	0.256	0.222	5.25	0.283	-	k_{PSO}	0.078	-	-	-	-	-	-
	W&M ID	-	-	-20.8	-	0.957	k_{ID1}	0.090	C1	2.05	k_{ID2}	0.015	C2	2.82
PUM	Avrami	0.024	0.021	-26.1	0.029	-	k_{AV}	1.55	n	0.102	-	-	-	-
	Elovich	0.023	0.020	-26.8	0.027	-	α	$5.47 \cdot 10^{11}$	β	17.8	-	-	-	-
	Fractional Power	0.023	0.019	-27.0	0.027	-	α	0.799	β	0.031	-	-	-	-
	PFO	0.212	0.207	2.15	0.251	-	k_{PFO}	0.309	-	-	-	-	-	-
	PSO	0.133	0.126	-4.37	0.157	-	k_{PSO}	0.317	-	-	-	-	-	-
	W&M ID	-	-	-20.2	-	0.748	k_{ID1}	0.018	C1	1.75	k_{ID2}	0.038	C2	1.64

F(t) indicated a slower enrichment for CHA compared to PUM. Specifically, PUM reached an $F(t) \geq 0.85$ after just 5 minutes of contact with $MnSO_4 \cdot H_2O$ solution, whereas CHA took 1 hour to reach $F(t) \geq 0.85$. Therefore, from a practical standpoint, PUM can be maintained in batch suspension for a few minutes to achieve a good enrichment in Mn^{2+} , while CHA requires a longer duration. In PUM, the rapid initial kinetic of Mn^{2+} enrichment, combined with the high Mn^{2+} sat. discussed in section 4.5.1, indicates a higher affinity of PUM for Mn^{2+} ions compared to CHA. Conversely, the adsorption capacity (q ; mg Mn^{2+} /g) of CHA was approximately 1.4 times greater than that of PUM, likely due to its higher content of zeolite minerals, specifically chabazite (Table 4.4). CHA exhibited strong correlations with the Weber-Morris Intraparticle diffusion and Elovich models (Table 4.5; Figure 4.9 B and C). The Weber-Morris model is the following equation [374]:

$$qt = kID \sqrt{t} + C$$

where kID (mg/g $\times$ min^{1/2}) is the kinetic rate constant, and C (mg/g) is a constant associated with the resistance to diffusion. Weber-Morris Intraparticle diffusion is a multi-linear process in which intraparticle diffusion limits adsorption or exchange. Each line has its own kID and C value, with higher C indicating a greater thickness of the boundary layer that hinders the

diffusivity of the chemical species (in this case, Mn^{2+}) within the porous structure of the material (in this case, zeolite mineral). Consequently, the mass transfer of Mn^{2+} within the porous structure of chabazite in CHA was likely limited by diffusion kinetic, which was not the case for PUM. In CHA, two distinct stages were observed; the second began around 2 hours of contact (as shown by the line on the right in **Figure 4.9 C**), where the diffusion through the boundary layer gradually slowed, approaching equilibrium condition. The first line had a C value of 2.05 mg Mn^{2+} /g, indicating that also during the first 2 hours of contact with the $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ solution, enrichment was constrained by surface layer diffusion.

The Elovich model is based on the following equation [375]:

$$qt = \frac{1}{\beta} \ln(1 + \alpha\beta t)$$

where α is the initial adsorption rate (mg Mn^{2+} /g $\times$ s) and β is a constant related to the extent of the surface coverage. Elovich kinetic is an empirical model which is commonly used in chemisorption; however, it has also been identified as a good predictor for the adsorption of heavy metals by clay minerals [376] and zeolites [377].

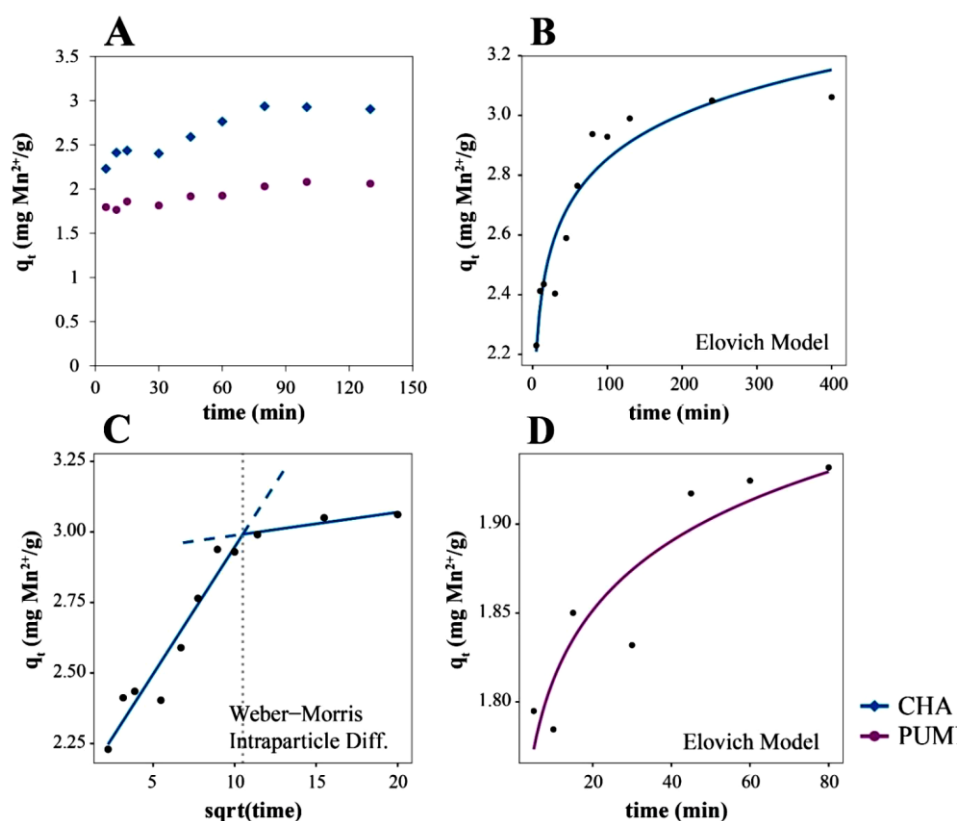


Figure 4.9. Kinetic data and modelling concerning the Mn^{2+} -enrichment of CHA and PUM. A) q_t (mg Mn^{2+} /g) vs. time (min); B) Elovich kinetic model for CHA; C) Weber-Morris Intraparticle Diffusion for CHA; D) Elovich model for PUM.

4.5.2 ISOTHERM MODELS

Considering equilibrium conditions, two distinct behaviors were observed in CHA and PUM (**Figure 4.10 A**). As expected, CHA achieved higher q_e values compared to PUM due to the higher amount of zeolite (**Table 4.4**). The shape of the isotherm also differed, as CHA likely exhibited a type II isotherm, while PUM showed a type I isotherm [378]. The larger variation in q_e values in CHA was $2.39 \text{ mg Mn}^{2+}/\text{g}$, while in PUM it was just $0.43 \text{ mg Mn}^{2+}/\text{g}$, indicating that PUM experienced conditions of semi-saturation for each point of the model. In other words, PUM achieved nearly the same q_e regardless of the solid to liquid ratio used, which is remembered to have been applied between 2.5 and 37.5% (w:v) in $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ at 1000 ppm of Mn. From an applicational perspective, this behaviour offers a significant advantage, as an industrial plant could utilize nearly any dosage of PUM relative to the batch volume of solution, achieving similar product characteristics in terms of Mn^{2+} enrichment. This indicates the good stability of PUM with respect to Mn^{2+} enrichment and therefore, ease in process prediction.

The average of the measured q_e of PUM was $1.46 \pm 0.18 \text{ mg Mn}^{2+}/\text{g}$, which was consistent with the t.CEC ($1.57 \text{ mg Mn}^{2+}/\text{g} = 0.173 \text{ mmol}(+)/\text{g}$).

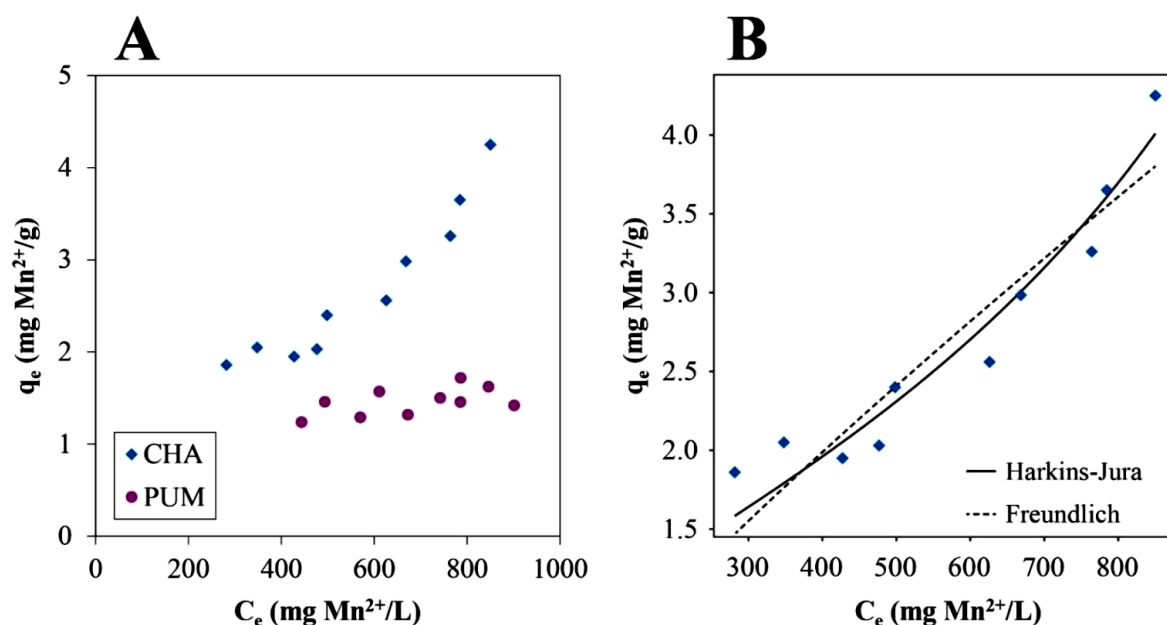


Figure 4.10. Equilibrium plots. A) q_e vs C_e plot for CHA and PUM; B) Harkins-Jura and Freundlich isotherm models for CHA.

While PUM exhibited slight variations in q_e , CHA demonstrated a significant increase at the rightmost part of the graph (**Figure 4.10 A**). This indicates that enrichment was facilitated by

lower solid-to-liquid ratios used. As anticipated, all q_e values for CHA were higher than those of PUM, with the maximum q_e recorded at 2.5% w:v dosage (4.25 mg Mn^{2+} /g) and the minimum at 37.5% (1.83 mg Mn^{2+} /g). In contrast to PUM, the type II shape of the isotherm of compels CHA to carefully control the solid/liquid ratio to allow accurate predictions of the enrichment in Mn^{2+} .

It was not possible to perform isotherm modelling on PUM due to the limited variation in q_e . The Harkins-Jura model showed the best correlation and significance ($0 < p\text{-value} < 0.001$) with the experimental data for CHA (**Table 4.6** and **Figure 4.10 B**). The model is expressed by the following equation [379]:

$$q_e = \left(\frac{AH}{BH - \ln C_e} \right)^{1/2}$$

where AH and BH are constants, and BH is related to the specific surface area of the material.

Harkins-Jura accounts for multilayer adsorption and is commonly applied in solids with a heterogeneous pore structure [380]. The structure of zeolites is ordered in a crystalline lattice, determining an ordered microporous structure; however, CHA being a natural material (zeolitized tuff) the presence of heterogeneous regions could be an option. For instance, the heterogeneity of the porous structure of a zeolite-rich rock (in this case, clinoptilolite) has been pointed out in [381]. Additionally, Harkins-Jura, as well as other multilayer isotherm models (e.g., Freundlich, also reported for CHA in **Figure 4.10 B**) have been demonstrated suitable for certain zeolite samples [236][334].

Table 4.6. Statistical parameters and equilibrium constants for the optimal fitting isotherm models for CHA. Statistical parameters are RMSE (Root Mean Square Errors), MAE (Mean Absolute Error), AIC (Akaike Information Criterion), SE (Standard Error) and the coefficient of determination (R^2). When * is present the p-values is between 0 and 0.001. p-value > 0.05 if no * is present.

Models	Statistics					Equilibrium constants	
	RMSE	MAE	AIC	SE	R^2		
<i>Freundlich</i>	0.271	0.235	8.27	0.031	0.879	$K_F = 0.0118$	$n = 1.17^*$
<i>Harkins-Jura</i>	0.195	0.172	1.69	0.038	0.939	$A_H = 5.79^*$	$B_H = 7.47^*$
<i>Henry</i>	0.256	0.223	7.15		0.890	$K_{HE} = 0.00393$	-

4.5.3 THE KINETIC OF Mn^{2+} RELEASE

The content of Mn occurring in virgin CHA and PUM was 0.77 and 1.08 mg Mn/g, respectively (**Table 4.4**). After the batch with $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, their content was 3.72 and 2.97 mg Mn/g, therefore the materials used in the release tests with the synthetic groundwater had a content of likely-exchangeable Mn^{2+} of approximately 2.95 and 1.89 mg Mn/g, respectively. However, despite the greater enrichment of CHA compared to PUM, CHA showed a lower capacity to release Mn^{2+} than PUM (**Figure 4.11 A**), whereas PUM released a higher proportion of Mn^{2+} , and showed superior release capacity (qt-rel; **Figure 4.11 A**).

Both CHA and PUM released only a fraction of the Mn^{2+} , equal to about 13.8% and 30.4%, respectively. By considering the composition of the synthetic groundwater, the concentration of positive charges (Na^+ , Mg^{2+} , K^+ and Ca^{2+}) approximatively accounted for 12.7 mmol(+)/L. The volume of solution used in each sample was 0.05 L, therefore 0.635 mmol of positive charges, potentially exchangeable with Mn^{2+} , were present. CHA and PUM were added (3 g), contributing to 8.84 and 5.68 mg of potentially exchangeable Mn^{2+} , meaning 0.161 and 0.103 mmol(+) represented by Mn^{2+} . Therefore, the number of charges of Mn^{2+} in CHA and PUM was significantly lower than the charges present in the solution. However, it is possible that the ionic strength of the synthetic groundwater was insufficient for allowing complete exchange, that was also beyond the scope of this study, which indeed aimed at verifying the release of Mn^{2+} in a realistic water intended for agricultural use.

Another difference was the speed in the release of PUM against CHA: after 15 minutes, PUM reached an $F(t)$ of 0.64 (with qt-rel = 0.346 mg Mn^{2+} /g) while CHA had a $F(t)$ of 0.30 (qt-rel = 0.106). In fact, $F(t)$, which is remembered to be equal to qt/qe, was initially steeper in PUM than CHA (**Figure 4.11 B**); then, CHA slowly converges to the values of PUM, reaching the same $F(t)$ after about 25-30 hours of contact with the synthetic groundwater.

The slower diffusivity of Mn^{2+} in CHA compared to PUM, should consider both the processes involved and the characteristics of Mn^{2+} in aqueous solution at the experimental conditions. Concerning the materials, the main active fraction in CHA is chabazite (with also possible minor contribution of the amorphous fraction). The mass transfer of Mn^{2+} is a multistage process that involves internal diffusion through the microporous structure of chabazite, boundary layer diffusion, and the diffusion from the boundary layer to the aqueous solution [382].

In the case of PUM, it is likely that most of the Mn^{2+} active sites were in the amorphous (i.e., glass) or semi-crystalline fractions, which constituted about 87.5 wt% of the material (**Table**

4.4). PUM showed greater affinity for Mn^{2+} and release capacity, however, for the purpose of this work, the adsorption and/or exchange processes were not mechanistically investigated, being the focus on the applicational perspective of PUM, simulating the environment of spraying machine tanks used in foliar fertilization.

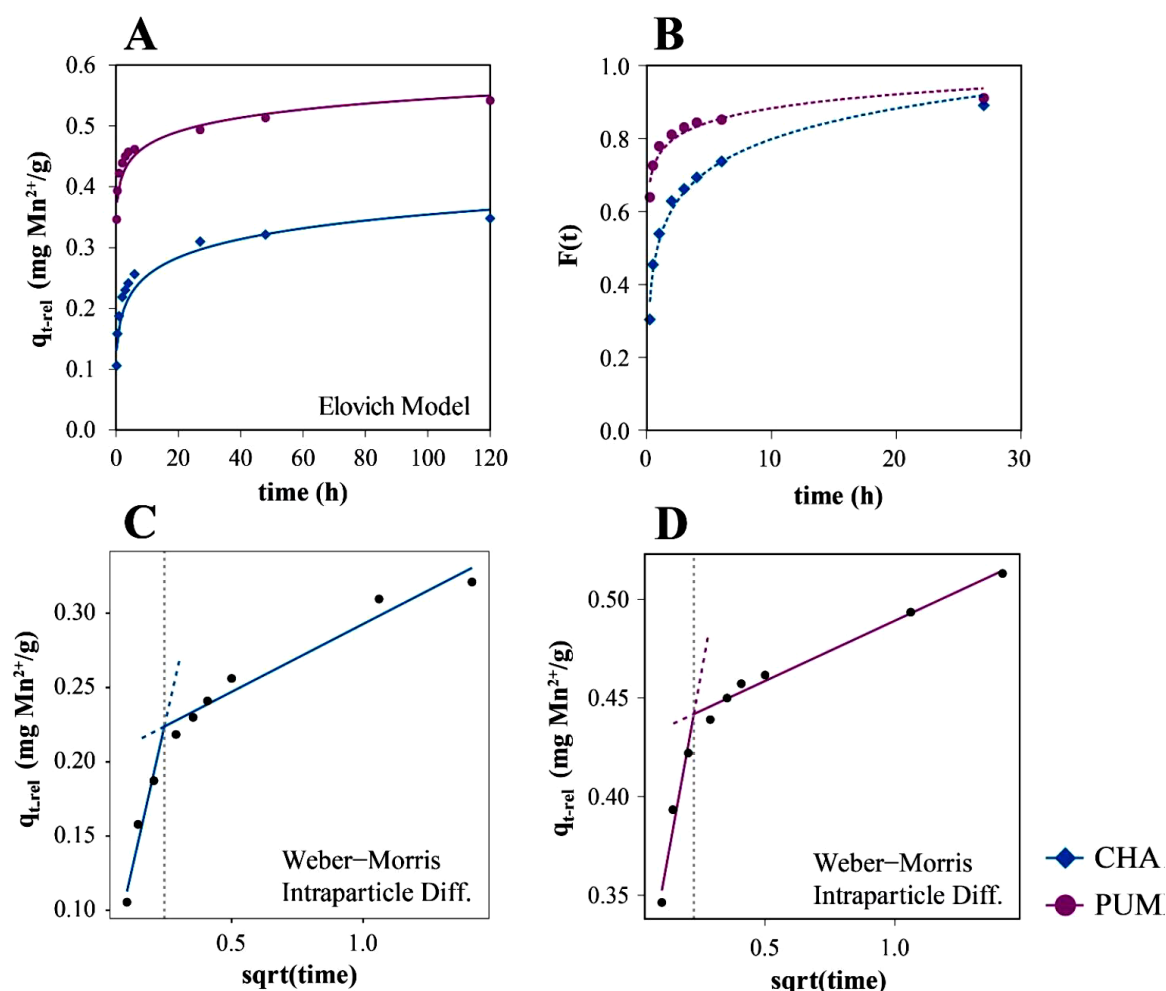


Figure 4.11. Release kinetics of Mn^{2+} in simulated groundwater by Mn^{2+} -enriched CHA and PUM. A) time-dependent capacity of Mn^{2+} release ($q_{t\text{-rel}}$), namely the mass of Mn^{2+} released per gram of material at time t , against time (h). Non-linear Avrami kinetic models for CHA and PUM are shown; B) Fractional uptake $F(t)$ against time (h). Lines are logarithm regression and are merely used for visualizing the trends of $F(t)$. Weber-Morris intraparticle diffusion model of CHA (C) and PUM (D) respect to Mn^{2+} desorption.

Besides the nature of materials, kinetics also depend on the chemical form of the Mn^{2+} . In aqueous solutions at room temperature, Mn^{2+} is coordinated by 6 water molecules, forming the Mn^{2+} -hexahydrate cation $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, from which monovalent cationic species are partially produced via hydrolysis of water molecules in the hydration shell, as follows: $\text{Mn}^{2+}(\text{H}_2\text{O})_6 \rightarrow (\text{MnOH})+(\text{H}_2\text{O})_5 + \text{H}^+$ [372]. Mn^{2+} therefore diffuses within the aqueous media by continuously exchanging water molecules with the environment, while maintaining a 6-coordination number.

Nevertheless, as chlorides and NaHCO_3 were used to prepare synthetic groundwater, in this study other ionic forms of Mn(II) could have developed, such as $[\text{Mn}(\text{H}_2\text{O})_6\text{-Cl}]^+$ and $[\text{Mn}(\text{H}_2\text{O})_6\text{-HCO}_3]^+$. In this context, the slower diffusion of Mn^{2+} in CHA respect to PUM, could have been related to the capacity of Mn^{2+} to form and disrupt hydrated cationic complexes and, in this case, with other anionic species present in the groundwater, in relation with the distinct nature of the materials. For both CHA and PUM, the optimal fitting kinetic models describing the release of Mn^{2+} in simulated groundwater were Elovich and Weber-Morris Intraparticle Diffusion. Statistical parameters and constants are reported in **Table 4.7**, while curves are shown in **Figure 4.11 A, C and D**.

Table 4.7. Statistical parameters and constants of Elovich and Weber-Morris Intraparticle Diffusion kinetic models respect to the release of Mn^{2+} simulated irrigation water for Mn^{2+} -enriched CHA and PUM. Statistical parameters are as follows: RMSE (Root Mean Square Errors), MAE (Mean Absolute Error), AIC (Akaike Information Criterion), SE (Standard Error) and the coefficient of determination (R^2), which is indicated only for the multi-linear Weber-Morris model and represents the overall coefficient of determination.

	Models	Statistics					Kinetic constants							
		RMSE	MAE	AIC	SE	R^2	param. 1		param. 2		param. 3		param. 4	
CHA	Elovich	0.010	0.010	-51.5	0.011	-	α	3.84	β	25.3	-	-	-	-
	W&M ID	-	-	-50.5	-	0.983	k_{ID1}	0.159	C1	0.033	k_{ID2}	0.019	C2	0.201
PUM	Elovich	0.011	0.009	-49.4	0.013	-	α	$53.6 \cdot 10^3$	β	35.2	-	-	-	-
	W&M ID	-	-	-59.4	-	0.988	k_{ID1}	0.148	C1	0.278	k_{ID2}	0.013	C2	0.428

4.5.4 POTENTIAL OF CHA AND PUM TO VEHICULATE Mn^{2+} TO CROPS AND PRELIMINARY COST OUTLOOK

The data discussed above highlight that CHA and PUM have substantially different behaviour. However, both the materials may be exploited synergistically in foliar film technology. The fast release of Mn^{2+} by PUM could indeed cope with incipient deficiencies, while the slow release by CHA would promote maintenance of the required nutrient level by preventing damage from excessive accumulation. The design of such a mixture would obviously require additional study and extensive trials in the field. In support of this consideration, previous studies showed that similar materials are capable of slow-release of nutrients when employed for foliar treatments [240][258][260][335] and in the soil [239][248][249][251].

As mentioned, pumice by-products are mostly reused for rehabilitation of quarry areas, but with additional costs for transportation. Or they can be stored in inland landfills but paying a fee when resold. A preliminary cost estimate can be based on the model already adopted in the

production of a zinc-based fertilizer [335], obtained considering the cost of producing atomized mixtures in ceramic tile industry.

Given the current costs of energy and manganese salt (about 4.75 €/kg), the production of a formulation consisting of 100% PUM enriched with Mn^{2+} is estimated to be approximately 1.95 €/kg (± 0.25 €/kg depending on plant production capacity). The costs of pumice scraps, likely attributable to collection and transportation, are not considered. On the other hand, as far as CHA is concerned, it is also necessary to consider the cost of the material, which is currently around 0.25 and 1.50 €/kg for grain sizes below 6 and 0.010 mm, respectively. These estimates, although preliminary, suggest that the production of Mn^{2+} -enriched CHA and PUM can be competitive with other traditional Mn-fertilizers, which range between 5 and 15 €/kg depending on the type, i.e., soluble salts, chelated, organometallic, etc. Moreover, there are additional economical and, most importantly, environmental benefits on PUM revalorization.

4.6 CONCLUSIONS

In this chapter, the potential use of volcanic raw materials has been discussed as carriers for the production of foliar fertilizers.

In the first part, a new foliar fertilizer formulation based on natural geomaterials rich in zeolites was proposed, with the aim of meeting both the demand for efficient Zn-based plant nutrition and the disposal of problematic quarry by-products. Zn plant deficiency relates to plant disease, human dietary deficit and health issues. Therefore, providing Zn to crops in case of inadequate plant uptake from the soil is necessary.

The best formulation, with unreduced properties respect to pure zeolitized tuff, comprised 70 wt% of zeolitized tuff and 30 wt% of pumice scraps. This formulation, for the same amount of Zn used, sprayed on plant of *Vitis vinifera* showed slower releasing properties and significative adhesion on leaves, proving better residence than traditional $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ fertilizer to rain leaching.

From the perspective of economic viability, net of environmental benefits, preliminary cost estimates suggest that $\text{ZT}^{70}\text{PU}^{30}$ can be placed in the market with competitive sales prices. Although possibly side effects are expected to be less than those experienced with conventional fertilizers, medium-to-large-scale agronomic assays will be needed before trade to demonstrate its true efficacy, absence of phytotoxicity and medium- and long-term impacts on

(micro)organisms. Similarly, a comparison with other slow-release foliar fertilizers (e.g., coated/encapsulated/chelated Zn compounds) is necessary both in terms of efficacy and cost-effectiveness.

Assuming an ever-increasing demand for Zn-based fertilizers, the development of methodologies for recovering and reusing Zn from wastewater could be an additional challenge for circularity which could nicely match with the outcome of this research.

In the second part, the use of pumice, often considered inert on the market, was investigated as a valuable resource for supplying manganese to crops through foliar application. Soil manganese deficiency in relation to crop requirements can lead to plant diseases, making the supply of manganese to crops essential in certain situations.

The behavior of zeolitized tuff and pumice was compared, and the latter showed a greater affinity for manganese, with a higher percentage saturation of cation exchange capacity, faster accumulation, and faster release in simulated groundwater. Although the overall enrichment of the pumice was significantly lower, the amount of manganese released was proportionally higher than that from the zeolitized tuff.

Both manganese-enriched zeolitized tuff and pumice have potential for slow-release applications; in fact, they can be combined to formulate mixtures with appropriate release kinetics, allowing for immediate release to meet urgent crop needs, followed by gradual release.

CONCLUSIONS AND FUTURE DEVELOPMENTS

The purpose of the present work was to test new and eco sustainable fields of application of national natural products belonging to volcanic minerals and related scraps. In the context of circular economy and valorization of national raw materials, numerous and different prototypes, belonging to different productive cycles, have been designed, created and characterized, in view of developing new commercial products (evaluation of a possible scale up). The choice fell in the following products: porcelain stoneware body, cementitious mortars and micronutrient-based fertilizers.

Ceramic bodies were developed within a collaboration with a company in the Sassuolo Ceramic District (Emilia-Romagna Region, Italy), CCV Ceramiche Castelvetro, by replacing imported feldspars with approximately 40-50% recycled materials, of which 10-16% consisted of volcanic by-products. Pumice and lapillus were successfully incorporated and served not only as fluxes but also as natural colorants due to the presence of chromophore elements such as iron (Fe) and titanium (Ti), identified by chemical analysis. The resulting products exhibited mechanical strength, water absorption and linear shrinkage values comparable to those of commercial ceramic products. In addition, their thermal expansion behavior is comparable to the existing glazes and engobes, allowing integration without altering the current industrial production process.

Compared to the reference formulation, the new mixtures showed several improvements: a significant reduction in the number of raw materials, a reduction in the water required for slurry preparation - especially in the lapillus-based mixture - and a significant reduction in the use of artificial colorants.

Starting from a previous study, ceramic bodies were formulated using German ball clay, which was gradually replaced by Italian kaolinitic clay. The aim was to create a ceramic body composed entirely of Italian raw materials. Two reference mixtures were considered: one based on volcanic lapillus scraps, and another based on pumice scraps. The replacement of German ball clay with Italian kaolinitic clay was evaluated in terms of both technological and aesthetic performance.

The Lapillus-based body showed low water absorption and relatively high linear shrinkage, especially in the sample with total substitution of German clay. This formulation also exhibited a microstructure similar to that of standard stoneware. This suggests that German ball clay can

theoretically be completely replaced, resulting in a body composed exclusively of Italian raw materials.

In contrast, pumice-based body with more than 50% Italian kaolinitic clay substitution showed water absorption close to the upper limit allowed for porcelain stoneware classification. Therefore, a partial replacement of German ball clay up to 25% is recommended to obtain technological properties comparable to those of commercial porcelain stoneware.

In both series, the internal microstructure of the samples changed. While the water absorption values suggest a classification within the BIa group, the ESEM analysis revealed an increased closed porosity and the presence of unreacted particles. The densification process occurred, as indicated by the increased linear shrinkage, but the water absorption did not reach zero. The lower plasticity of the Italian kaolinitic clay may account for the increased porosity. Therefore, although complete substitution is technically feasible in Lapillus-based blends, it is advisable to retain a portion of German ball clay to control pore formation and improve the technological properties of the final product.

To complete the study on porcelain stoneware, the life cycle assessment of three products was performed during the internship abroad in Spain at University of Jaen (Department of Chemical, Environmental and Materials Engineering, of the Higher Polytechnic School of Linares): the reference product (porcelain stoneware currently on the market), pumice-based porcelain stoneware, and lapillus-based porcelain stoneware.

The inventory analysis assessed the environmental impacts associated with raw material extraction, transportation, and product manufacturing, highlighting that transportation accounted for over 95% of the total impact in all scenarios. This was followed by the manufacturing phase, with a minimal contribution from raw material extraction. In scenarios using volcanic scrap materials, impacts decreased in all categories, with reductions ranging from approximately 8% (for aquatic ecotoxicity) to nearly 48% (for acidification). Despite the domestic origin of materials, road transport remained a major contributor to environmental impacts, exacerbated by the low energy impact of the plant due to its near self-sufficiency. Suggested improvements include the use of rail transportation and sourcing materials closer to the production site. While comparison with existing literature proved challenging, the study confirmed the high impact of transportation and demonstrated that pumice- and lapillus-based tiles not only perform well technologically but also offer notable environmental and health

benefits over conventional products. These results support the sustainable use of volcanic waste in porcelain stoneware production.

The study on the incorporation of volcanic raw materials into a porcelain stoneware body was initially performed in a ceramic company but on a laboratory scale. The research was later scaled up to a pre-industrial level, which revealed the need for certain adjustments to the original formulations. The company has expressed its intention to carry out a full-scale industrial trial as soon as possible to evaluate further optimizations before moving towards potential production. Pumice and volcanic lapillus proved to be excellent fluxes, capable of imparting good technological properties to the final product. Although they cannot completely replace the fluxes currently used, they are promising raw materials, especially for the production of colored ceramic bodies.

Volcanic lapillus was used as a supplementary cementitious material (SCM), replacing both CEM II 42.5 and CEM I 52.5, and as a substitute for standard sand. When used as an SCM, compressive strength increased with curing time. However, mechanical strength declined when lapillus content exceeded 10%, indicating that while lapillus shows pozzolanic activity, it is less effective than cement in terms of early strength development.

SEM analysis of mortars containing 20% lapillus revealed a less dense structure compared to the reference. Over 28 days of curing, improvements in compactness and adhesion between the cementitious gel and aggregates were observed, alongside a reduction in porosity. Additionally, lapillus use reduced alkali-silica reaction (ASR) potential and improved sulfate resistance by limiting the formation of expansive compounds.

Regarding chloride penetration, 10% lapillus-substituted samples performed comparably to the control, whereas 15% substitutions showed higher permeability, consistent with increased porosity. Capillary water absorption tests confirmed this trend. A reduction in calcium hydroxide content in modified samples supported the occurrence of pozzolanic reactions over time.

Although only a preliminary evaluation was conducted on CEM I 52.5, lapillus showed promise as a SCM.

The use of lapillus in substitution of sand led to an increase in porosity and a marked reduction in the mechanical strength of the material, especially in the early days of curing. However, with longer curing times, a slight improvement in material properties is observed due to the

progressive reaction between the lapillus and the cement matrix. To optimize performance, it would be useful to reduce the water/cement ratio to improve the density and durability of the compound. However, it would be better not to replace the normalized sand with volcanic lapillus, which has been found to be a good SCM.

The research based on the replacement of cement or sand with lapillus was carried out in collaboration with Cismondi srl (Piedmont, Italy), a laboratory authorized by the Ministry of Infrastructure and Transport to carry out and certify tests on innovative cementitious building materials. The use of lapillus as a supplementary cementitious material (SCM) has shown very promising results. The growing need for cement plants to reduce CO₂ emissions has encouraged the search for new raw materials that can replace, at least partially, clinker in cements. In addition, other companies have expressed interest in starting experiments in this area.

Research on micronutrient-based fertilizers developed within the University of Modena and Reggio Emilia (Department of Engineering “Enzo Ferrari” and Department of Chemical and Geological Sciences) has demonstrated the promising potential of volcanic materials—particularly zeolite-rich geomaterials and pumice scraps—as effective and sustainable carriers for essential nutrients like zinc (Zn) and manganese (Mn) in foliar applications. Zinc deficiency is a well-known cause of plant diseases and, indirectly, of nutritional imbalances in the human diet. However, conventional Zn-based fertilizers often suffer from low efficiency, primarily due to poor absorption and leaching losses. In this context, a new fertilizer formulation was developed, combining 70% natural zeolitic tuff with 30% pumice scrap. This blend not only retains the beneficial properties of pure zeolitic tuff but also improves the product’s performance. When applied to *Vitis vinifera* (grapevine) plants, this formulation exhibited slower release rates and better adhesion to leaves, significantly enhancing resistance to rain-induced leaching when compared to traditional ZnSO₄·6H₂O fertilizers. These properties suggest more effective and longer-lasting Zn availability to plants.

From an economic perspective, preliminary evaluations indicate that this formulation could be marketed at competitive prices, even without factoring in the additional environmental benefits. This makes the approach attractive both from a commercial and ecological standpoint.

In parallel, a feasibility study was conducted to explore the use of volcanic pumice as a carrier for manganese (Mn²⁺), another essential micronutrient. Manganese deficiencies in soil can severely affect crop health and yields, making targeted supplementation necessary in certain

agricultural contexts. Although often considered inert in industrial applications, pumice proved to be a valuable carrier in this setting. It demonstrated a higher cation exchange capacity saturation, quicker metal uptake, and faster release into simulated groundwater compared to zeolitic tuff. While the total Mn content absorbed by pumice was lower, the proportion actually released was significantly higher, highlighting its efficiency in delivering usable nutrients to plants.

Both manganese-enriched zeolite tuff and pumice offer excellent prospects for controlled-release formulations. Their complementary release kinetics allow for nutrient delivery that meets both immediate and long-term crop needs, thus supporting more efficient and sustainable fertilization strategies.

The Zn-based formulation has attracted the interest of some companies, making it possible to start a trial on a pre-industrial scale in the near future. As for the Mn-based formulation, however, it will be necessary to continue with more in-depth studies and define optimal compositions for experimental testing. Nevertheless, the data collected so far indicate that this is a promising application, with good prospects also from an economic point of view.

As a general conclusion, it can be stated that volcanic minerals, and in particular their scraps, provide a valuable resource for diversified applications. Their use has been shown to reduce environmental impact compared to conventional products, while revitalizing the domestic raw materials market. These developments contribute to making the Italian economy more resource efficient and less dependent on foreign materials.

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Article

Characterization of Volcano-Sedimentary Rocks and Related Scraps for Design of Sustainable Materials

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Abstract: This work started as a joint academia and company research project with the aim of finding new applications for domestically sourced volcanic products and related waste (pumice, lapillus, zeolitic tuff and volcanic debris from Tessennano and Arlena quarry) by creating a database of secondary volcanic raw materials and their intrinsic characteristics to help industry replace virgin materials and enhance circularity. In this context, accurate chemical, mineralogical, morphological, granulometric and thermal characterizations were performed. Based on the results presented, it can be concluded that due to their lightness, these materials can be used in the design and preparation of lightweight aggregates for agronomic purposes or in the construction field. Furthermore, due to their aluminosilicate nature and amorphous fraction, pumice and lapillus can play the role of precursor or activator for geopolymer preparation. With its porous nature, zeolitic tuff can be exploited for flue gas treatment. Due to the presence of feldspathic phase (sanidine), these materials can be used in tile production as a fluxing component, and with their pozzolanic activity and calcium content, they have application in the binder field as supplementary cementitious material or as aggregates.

Keywords: volcanic rocks; volcanic scraps; materials



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1. Introduction

Volcanic products are available in considerable quantities in many regions of the Earth and constitute a valuable natural and, in most cases, ecological resource, but are not fully exploited despite their enormous potential.

These raw materials are aluminosilicate-based, and their main field of application is horticulture. Volcano-sedimentary rocks can be, although to a lesser degree than in horticulture, applied in a variety of fields, such as the production of concretes, ceramic materials, insulators, adsorbents, etc. Many applications are reported in the literature, depending on the type and chemical composition of the specific material [1–3]. This study focuses on pumice, lapillus, zeolitic tuff, Tessennano and Arlena debris extracted from various quarry sites in Italy.

Pumice is a naturally expanded magmatic alveolar rock that originates from explosive volcanic eruptions following a violent expansion of dissolved gas in lavas of acid chemical composition. The rapid cooling of the rock prevents it from crystallizing, causing the gases dissolved within it to expand and generate a glassy foam. The inside of the rock is in fact composed of a huge number of small to medium diameter channels, interconnected with each other and with the outside [4]. This process forms a natural and environmentally friendly product, which is very dimpled; therefore, it is light, with high porosity, high water retention, slow liquid release and high thermal and acoustic insulating power.

The properties of pumice have been known for a long time; in fact, there are many studies in the literature on the use of pumice in various areas. In horticultural applications,

pumice can be used as an inorganic component in substrates for green roofs, together with various organic compounds, thereby improving the chemical and physical properties of the soil, plant growth and nutrient supply and decreasing the stress to which plants are subjected [5,6]. In the same field, other authors studied the possibility for pumice to be engineered and used in the structure of a fertilizer [7], and Kong et al. investigated its use as a soil improver [8]. Pumice is also highly valued in the building industry, as it is used in concrete and mortar to achieve thermal insulation, fire resistance, freeze/thaw resistance, chemical resistance, reduction in the expansion of the alkali–silica reaction and lightness of the matrix [9]. More recently it has been studied for the production of alkali-activated materials [10–12]. Other fields of application for pumice can also be found in the literature, such as use as a biofilter for the removal of nitrogen from a recirculating aquaculture system [13] or as a combined medium for the purification of domestic wastewater [14,15].

Volcanic lapillus is an effusive magmatic rock (Pleistocene Vulsini Volcanite) that originates from explosive volcanic eruptions following a violent expansion of dissolved gases in lavas of acid chemical composition, as with the formation of pumice. Volcanic lapillus forms from magma with a lower silica content than that which forms pumice. The lower viscosity and slower cooling of the lava facilitates the escape of a certain amount of gas from the magma. This leads to the formation of rocks characterized by voids with a larger average diameter than those of pumice, but they are far fewer in number. It is an inert natural volcanic, naturally calcined at high temperature, porous, insulating, light and free of toxic and hazardous substances.

The properties of lapillus, compared with pumice, are less well known, but it is a suitable material in technical green areas for creating drainage, and is ideal for lawns and sports facilities. It is also used in construction as a thermal and acoustic insulator and for rehabilitating masonry and reinforced concrete works [16], and some authors have studied its alkaline activation for the manufacture of geopolymers [17].

Zeolitic tuff is a volcanic product with high and selective cationic exchange power and has the capacity to neutralize, by retaining them in its structure, leachable elements such as ammonium, heavy metals and organic molecules, and to absorb odorous gases such as ammonia, hydrogen sulfide and mercaptans.

Among the materials mentioned so far, zeolites and zeolitic products are the most studied; they are of great use in the agricultural field as they improve the physical characteristics of soil and make it possible to reduce the use of synthetic fertilisers as well as irrigation water. They minimize NO_3 -leaching from soil and optimize crop growth and yield. In fact, numerous applications can be found, for example, in wheat, rice crops and maize [18–20], and in the oenological field [21]. They have also been investigated as an adjunct to fertilisers [22,23]. Due to their high adsorbing and filtering power, they can also be used for decontaminating heavy metals [24,25] and for removing harmful elements from wastewater [26]. In addition, there are examples of their use in construction for the manufacture of high-performance self-hardening concretes [27] and in cementitious materials [28], where the addition of zeolite improves certain properties.

In this paper, the rocks and debris mentioned were subjected to chemical-physical, mineralogical, thermal and microstructural characterisation, and compared in order to investigate their potential application (alone or mixed with each other or mixed with other raw materials) in tailoring of new products useful in different fields, including construction, agronomy and industrial emission management. In the literature, there are no papers simultaneously highlighting and comparing the physical-chemical-thermal-morphological properties of these natural minerals (and their possible extraction scraps). Therefore, the aim of the paper is to create a database of secondary volcanic raw materials and their intrinsic characteristics to help industry use them to replace virgin materials and, thereby, enhance circularity.

2. Materials and Methods

2.1. Volcanic Products

Volcanic rocks are extracted from quarries in the territory between the Vulsino Volcanic District (extending from southern Tuscany to northern Lazio around Lake Bolsena) and the Cimino–Vicano Volcanic District (around Lake Vico, further south than the previous one).

Latium volcanoes belong to two clearly different magmatic series. The first includes the acidic, rhyolitic and rhyodacites volcanism of the Cimino, Tolfa and Ceriti Mountains and is older than the second series which includes the Vulsino, Vicano, Sabatino and Colli Albani groups, and shows a strongly alkaline-potassium nature. Latium, therefore, represents the junction area of these two different systems [29].

The pumice, lapillus, zeolitic tuff and debris from the Tessennano and Arlena quarries used in this work were supplied by Europomice srl. Pumice is mined in Tuscany, in Pitigliano (GR) at ‘Poggio Nardecì’, and in Latium, in Tessennano (VT) at ‘Riserva Muraccio’ and Arlena di Castro (VT). Lapillus and zeolitic tuff are mined in Latium in Cellere (VT) at “Monte Cellere” and in Tessennano (VT) at “Riserva Muraccio”, respectively. Tessennano and Arlena debris are mined in quarries in northern Latium. Arlena and Tessennano sands are the scrap from the processing of pumice, hereafter called sands for simplicity.

Figure 1 shows the Pitigliano pumice quarry (Figure 1a) and a sample (Figure 1b) characterized by a matrix within which are embedded pumiceous clasts that exhibit gray coloration. The sample also has elongated pseudo rectangular transparent crystals, probably potassium feldspar. Figure 2 shows a lapillus sample (Figure 2a) and zeolitic tuff (Figure 2b).



Figure 1. Pitigliano pumice quarry (Grosseto, Tuscany) on the **left** (a) and pumice stone on the **right** (b) [16].



Figure 2. Lapillus (a) and zeolitic tuff (b) [16].

All the materials used in this study, except the zeolitic tuff, are quarry scraps.

2.2. Chemical and Physical Characterization

Approximately 1000 g of a well-mixed sample was taken from each mineral in order to ensure a representative sample of the entire bank of material. The samples were subjected

to particle size analysis, pH and specific conductivity measurements, true density, chemical and mineralogical analysis, and finally investigated with a scanning electron microscope (SEM). Before performing the analyses, the samples were dried in an oven for 24 h at a temperature of 100 ± 5 °C.

The particle size analysis was performed by taking 100 g of sample and sieving it first manually, using stacked sieves with an average hole diameter of 2 mm and 1 mm, to separate the coarse fraction from the fine one. The analysis was then performed with a laser particle size analyzer (Malvern Instruments (Malvern, UK), model Hydro200S).

In order to evaluate the chemical stability of the samples by assessing the release of ions into the aqueous environment, pH and specific conductivity measurements were carried out using a portable pH tester (Laboratory PH sensor Hamilton type Liq-glass SL, OAKTON Eutech Instruments (Vernon Hills, IL, USA) pH 5/6 and Ion 6) and a portable conductivity tester (OAKTON Eutech Instruments CON6/TDS 6, Vernon Hills, IL, USA), respectively. A few grams of sample were taken and placed inside a beaker containing bi-distilled water with a sample–water ratio of 1:10. The test was performed in dynamic mode (700 rpms) for 8 h; measurements were taken at predetermined times, i.e., at the initial instant and after 5, 15, 30, 60, 120, 240 and 480 min. The above reported procedure is in accordance with UNI EN 13037:2012 (pH rule standard) and UNI EN 13038:2012 (conductivity rule standard).

True density (ρ_{abs}) measurements were assessed for each mineral with a helium pycnometer (Mycromeritics Accupyc 1340, Norcross, GA, USA) by taking a few grams of sample and placing them inside a 10 cm³ measuring cell. Bulk density (ρ_{bulk}) was measured by Geopyc 1360 Envelope Density Analyzer (Micromeritics, Norcross, GA, USA). In this analysis, the sample is placed in a cylindrical chamber equipped with a piston. The measure is run before with the empty chamber to determine the total volume and after with the granular sample. The volume of the sample is determined by subtracting the volume of the empty chamber from the volume of the same chamber after the sample has been added.

The chemical analysis was performed by sequential X-ray Fluorescence Spectrometer (XRF) using an ARL PERFORM'X instrument, and the mineralogical analysis was performed by X-ray diffraction with the Rietveld method using an X'PERT 3 POWDER PANALYTICAL instrument. The phase fractions were extracted by the Rietveld refinements, using GSAS software and they were rescaled on the basis of the absolute mass of corundum originally added to the mixtures as an internal standard. The chemical and mineralogical analyses were provided by the volcanic raw material company.

Microstructural analysis was conducted using an environmental scanning electron microscope (ESEM), model ESEM-Quanta 200, coupled with an X-ray EDS microanalysis system, model X-EDS Oxford INCA-350, to perform the chemical analysis (on lapillus and pumice only).

2.3. Thermal Characterization

In order to investigate the possible fields of use of the materials, their thermal transformations were studied by thermo-gravimetric and differential thermal analyses (TGA/DTA) and hot stage microscopy (HSM).

The samples were appropriately ground with an agate mortar to avoid possible contamination and powdered, reaching an average particle diameter of less than 20 µm. The samples were analyzed with a heating rate of 10 °C/min.

DTA allows determination of the thermal reactivity of the powders as the temperature increases, while TGA determines the change in mass as a function of temperature resulting from the development or absorption of gases. The TGA/DTA analyses were performed simultaneously with the NETZSCH STA 429 (CD) instrumentation.

The HSM analysis was performed with Expert System Solutions instrumentation, model M3MD1600/80/2. The samples were first reduced to powder and then pressed to form very small cylinders 2 mm in diameter and 3 mm in height. Images were taken at a heating rate ramp of 10 °C/min until 1300 °C. During the post-analysis phase, by means

of calculations on the shape of the specimen, the instrument software is able to attribute the characteristic temperatures of the transformation states (sintering, softening, sphere, hemisphere and melting temperatures) for each sample analyzed.

3. Results

3.1. Chemical and Physical Characterization

3.1.1. Particle Grain Size Analysis

The data obtained for the sample fraction less than 1 mm are represented by two curves on a semi-logarithmic scale: a cumulative curve (whose corresponding y-axis is on the right-hand side), and a bimodal distribution curve. The characteristic diameters are also shown.

Lapillus presented the following particle size distribution: 6.5% of particles had diameters greater than 2 mm, 17% had diameters between 1 mm and 2 mm, and the remaining 76.5% had diameters of less than 1 mm. The fraction with a diameter of less than 1 mm is visible in Figure 3. Based on the reported data, 90% of the distribution is under 65 μm and 100% is under 753 μm . The D50 value indicates that the 50% of the distribution was under 22 μm .

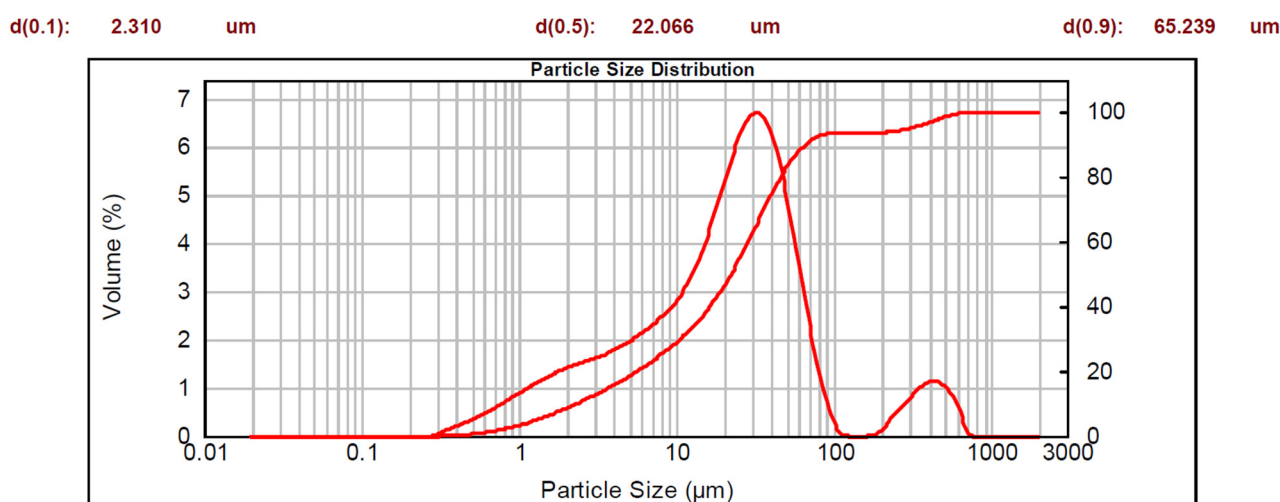


Figure 3. Particle size distribution of lapillus.

Pumice presented the following particle size distribution: 27% of particles had diameters greater than 2 mm, 31% had diameters between 1 mm and 2 mm, and the remaining 42% had diameters of less than 1 mm. The fraction with a diameter of less than 1 mm is visible in Figure 4. Based on the data reported, 90% of the distribution is under 278 μm and 100% is under 851 μm . The contrasts with the distribution for lapillus, for which only 81% of the sample was under 65 μm . The D50 value indicates that the 50% of the distribution was under 22 μm .

Arlena sand presented the following particle size distribution: 15% of particles had a diameter greater than 2 mm, 15.5% had a diameter between 1 mm and 2 mm, and the remaining 69.5% had a diameter of less than 1 mm. The fraction with a diameter of less than 1 mm is visible in Figure 5 where the 50% of the distribution is less than 30 μm .

Tessennano sand presented the following particle size distribution: 33% of particles had a diameter greater than 2 mm, 23% had a diameter between 1 mm and 2 mm, and the remaining 44% had a diameter of less than 1 mm. The fraction with a diameter of less than 1 mm is visible in Figure 6. The D90 value was 561 μm , and the D50 was 76 μm .

The particle size distribution of the sands indicates that the material is coarser than lapillus and pumice.

The particle size analysis was not performed on zeolitic tuff because the grain size depends on its use, so the material is ground by the company to the required size. The

sample extracted from the quarry presented a large grain size range (from 7–35 mm up to 1–100 μm).

d(0.1): 2.627 um d(0.5): 22.044 um d(0.9): 278.499 um

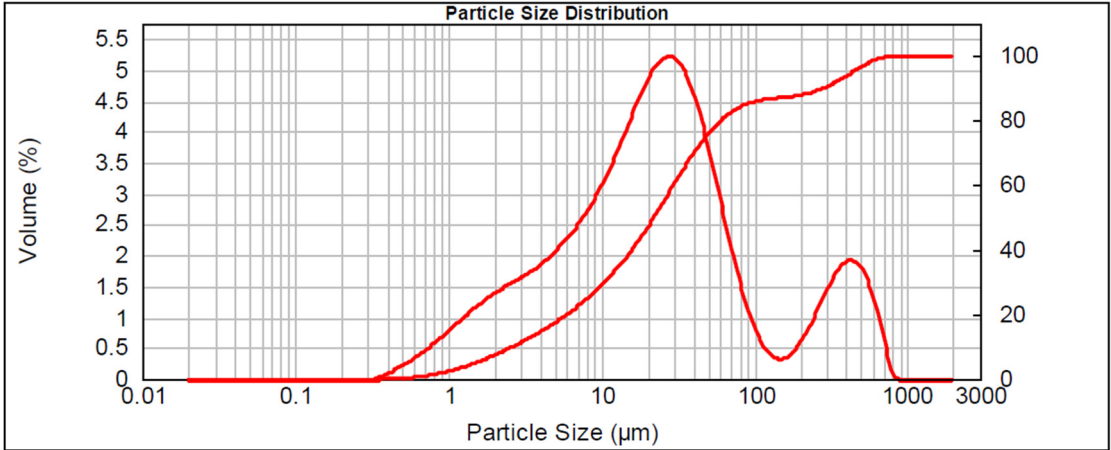


Figure 4. Particle size distribution of pumice.

d(0.1): 3.830 um d(0.5): 30.987 um d(0.9): 409.366 um

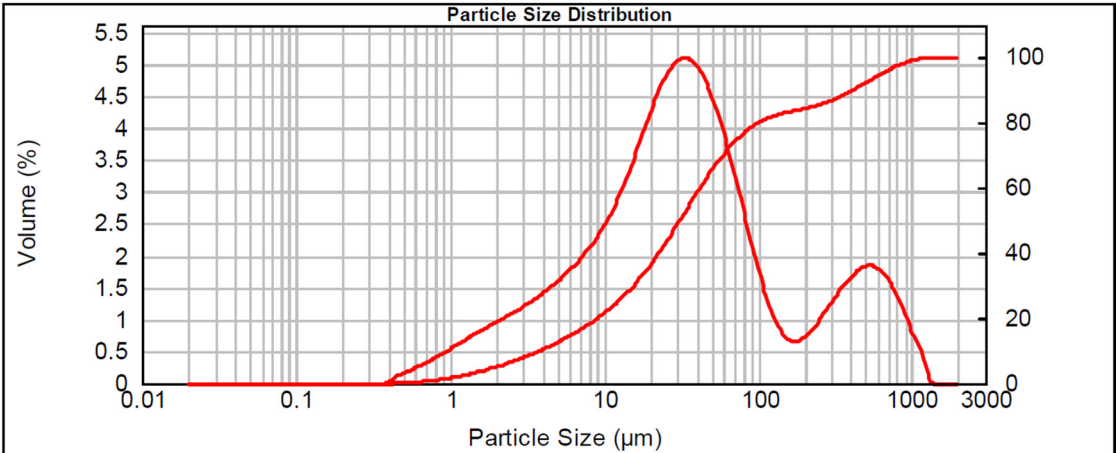


Figure 5. Particle size distribution of Arlena sand.

d(0.1): 7.140 um d(0.5): 76.023 um d(0.9): 561.296 um

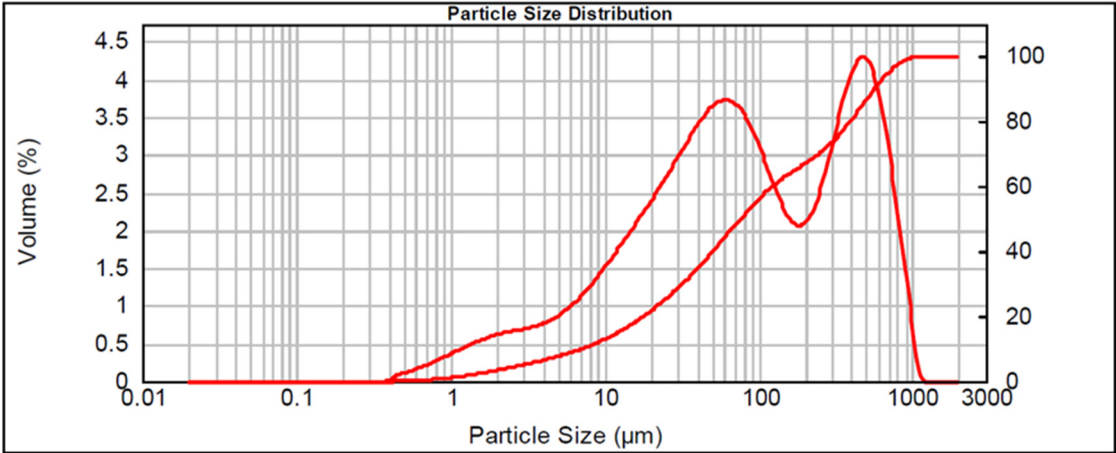


Figure 6. Particle size distribution of Tessennano sand.

3.1.2. Chemical and Mineralogical Analyses

The results of the XRF analysis shown in Figure 7 indicate that the materials have an aluminosilicate character.

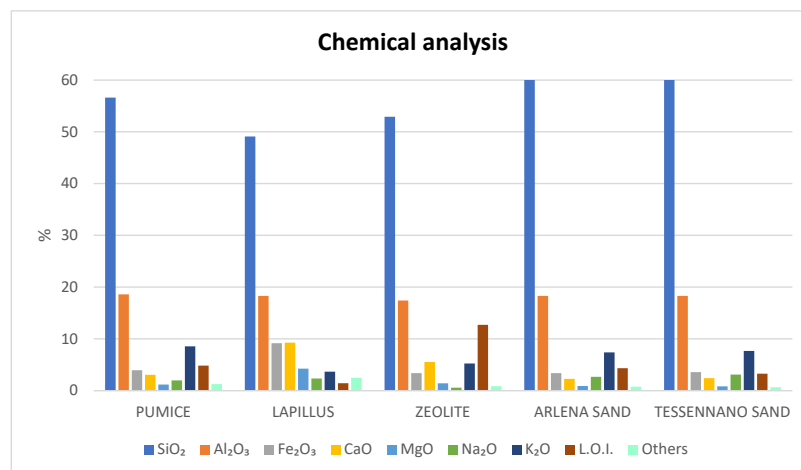


Figure 7. Chemical analysis (XRF) in wt% oxide of all the volcanic products.

The highest SiO₂ content was observed in the two sands (around 60%).

Fe₂O₃, CaO, MgO, K₂O and Na₂O were detected in all materials. Lapillus had a higher Fe₂O₃ and CaO content than the other materials. With the exception of lapillus, in all the other volcanic products, K₂O varied between about 5.2% and 8.5%. The two sands presented a very similar chemical composition. In the zeolitic tuff, the content of Na₂O was very low. Loss of ignition of zeolitic tuff is higher than for the other materials due to its characteristic content of water. The chemical data are in line with the literature for pumice, with SiO₂ and Al₂O₃ levels of 48% and 14.9%, respectively. Moreover, an appreciable iron oxide content (6.71%) was observed. Other oxides, such as MgO, Na₂O, CaO and K₂O, were also detected [30].

The mineralogical analysis (Table 1) showed that all the products under investigation exhibited an amorphous fraction; this was very low in zeolitic tuff and lapillus and very high in pumice and sands. Zeolitic tuff was similar to pumice in terms of the amount of quartz detected. It is close to lapillus in terms of the amount of amorphous fraction detected and, like the two sands, showed a small percentage of biotite. Sanidine and anorthite were detected in pumice, lapillus, and in Arlena and Tessennano sands. Muscovite and phlogopite were only detected in the pumice, while hematite, plagioclase and mica only in the lapillus. Tessennano sand was the only material analyzed that did not contain analcime. Arlena sand and zeolitic tuff showed 9% and 54% of chabazite, respectively.

Table 1. Quantitative mineralogical analyses (wt%).

Mineralogical Phase	Lapillus	Pumice	Zeolitic Tuff	Arlena Sand	Tessennano Sand
Amorphous	16.1	79.7	11.0	61.7	78.2
Quartz (SiO ₂)	-	1.1	1.0	3.5	2.0
Sanidine (K,Na)(Si,Al) ₄ O ₈	19.8	11.2	-	18.2	16.0
Anorthite (CaAl ₂ Si ₂ O ₈)	26.4	3.0	-	3.2	3.0
Biotite (K(Mg,Fe ₂₊) ₃ (AlSi ₃ O ₁₀ (OH,F) ₂)	-	-	6.0	0.5	0.8
Chabazite (Ca,Na ₂ ,K ₂ ,Mg)Al ₂ Si ₄ O ₁₂ ·6H ₂ O	-	-	54.0	9.4	-
Phyllipsite (Ca,Na ₂ ,K ₂)Al ₆ Si ₁₀ O ₃₂ ·12H ₂ O	-	-	6.0	-	-
Analcime (NaAlSi ₂ O ₆ ·H ₂ O)	6.1	0.6	1.0	1.0	-
Pyroxenes	-	-	2.0	-	-
Feldspars	-	-	19	-	-
Diopside (CaMgSi ₂ O ₆)	19.0	-	-	2.5	-
Muscovite (KAl ₂ (Si ₃ Al)O ₁₀ (OH,F) ₂)	-	3.8	-	-	-
Phlogopite (KMg ₃ (Si ₃ Al)O ₁₀ (F,OH) ₂)	-	0.6	-	-	-
Hematite (Fe ₂ O ₃)	4.9	-	-	-	-
Plagioclase (Na,Ca)(Si,Al) ₄ O ₈	5.8	-	-	-	-
Mica X ₂ Y ₄₋₆ Z ₈ O ₂₀ (OH,F) ₄	1.9	-	-	-	-

3.1.3. pH, Specific Conductivity and Density

The pH and specific conductivity were measured under stirring conditions and their trends are reported in Figures 8 and 9. Based on these plots, it is evident that the pH values were all very similar and near to neutrality. On the other hand, the conductivity showed more significant differences among the different volcanic materials and an increasing trend with time.

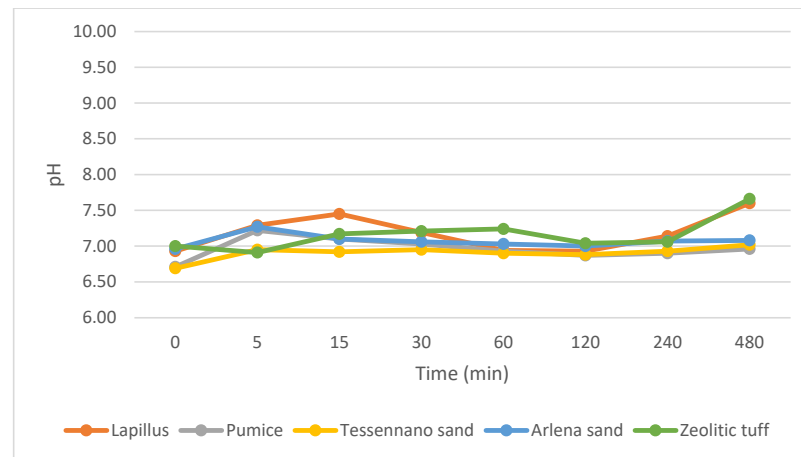


Figure 8. pH under stirring condition.

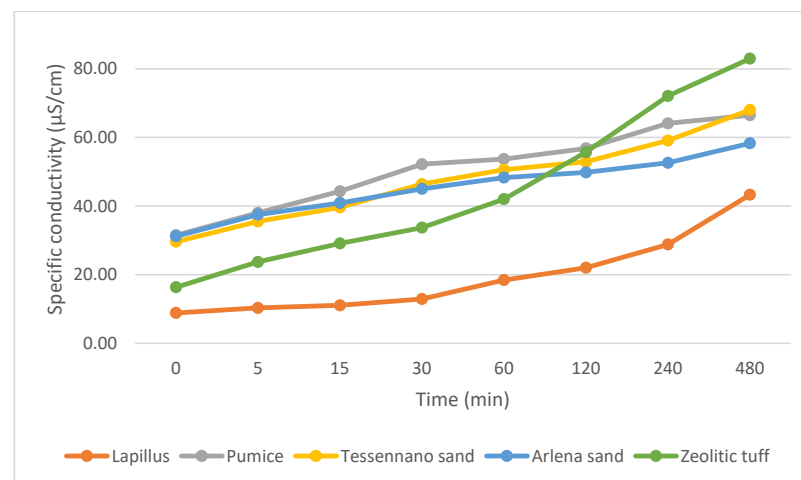


Figure 9. Specific conductivity under stirring condition.

The true and bulk density values for each material can be seen in Table 2.

Table 2. True and bulk density data for all the rocks analyzed.

Samples	True Density (kg/m ³)	Bulk Density (kg/m ³)
Lapillus	2843.8 ± 0.6	750–1150
Pumice	2579.3 ± 1.6	480–880
Zeolitic tuff	2284.3 ± 1.1	700–1000
Arlena sand	2475.0 ± 0.8	900–1100
Tessennano sand	2435.2 ± 1.0	900–1100

True density corresponds to the mass of a particle divided by its volume, excluding open and closed pores. Generally, this kind of density depends on the chemical compositions of the volcanic products. Zeolitic tuff showed a lower true density value than the other

products, while the two sands presented very similar values. Lapillus showed a higher density value than the other volcanic rocks while pumice showed an intermediate value.

The bulk density of a powder is the ratio of the mass of an untapped powder sample and its volume including the contribution of the inter particulate void volume. Hence, the bulk density depends on both the density of powder particles and the spatial arrangement of particles in the powder bed.

The bulk density values measured on volcanic products show that pumice is the lighter material. This indicates the presence of intraparticle and interparticle porosity; therefore, lower values were observed for more porous and lighter materials, such as pumice, lapillus and zeolitic tuff, with respect to the sands.

3.1.4. SEM Analysis

The SEM analysis was performed on the pumice and lapillus samples only.

The microstructural analysis of lapillus sample (Figure 10) showed:

- A wide grain size range between 20 and 400 μm ;
- Low mutual densification between particles;
- Particles with irregular shapes and jagged edges;
- High interparticle porosity regardless of particle size.

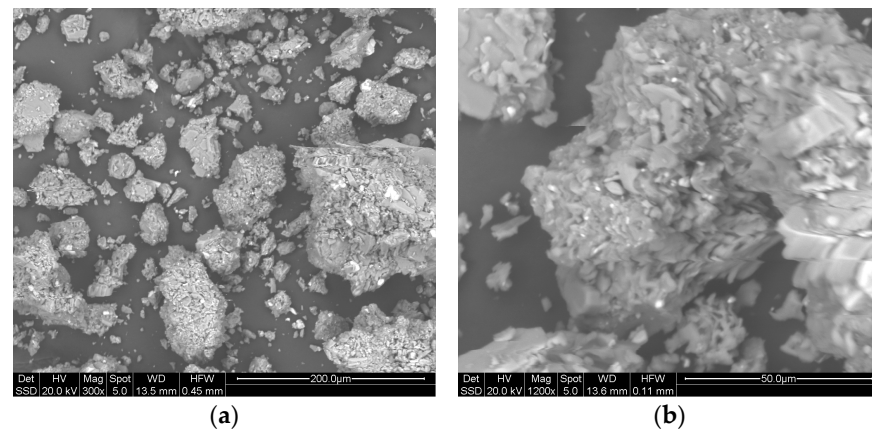


Figure 10. Lapillus: micrographs at 300 $\times$ (a) and 1200 $\times$ (b) in backscattered electron (BSE) mode.

The microstructural analysis of the pumice sample (Figure 11) showed:

- A high proportion of particles with sizes in the range 100–200 micron;
- Particles with a more regular shape than those of the lapillus sample;
- Greater interparticle thickening;
- Presence of non-porous glassy zones (circled in Figure 11b) corresponding to the vitreous fraction detected by XRD (79.7%).

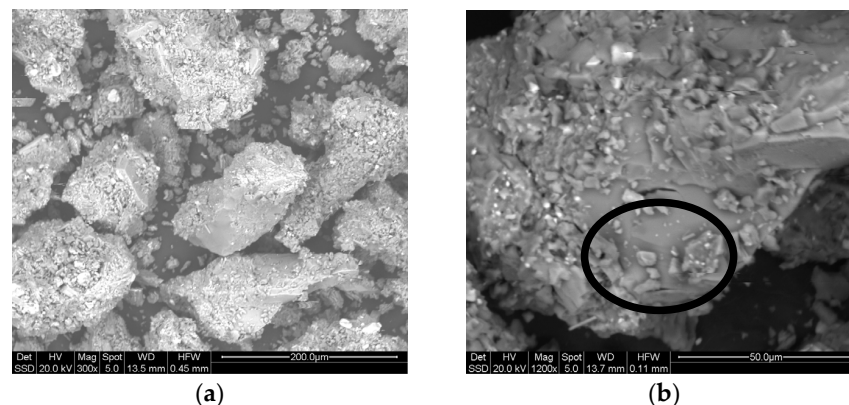


Figure 11. Pumice: micrographs at 300 $\times$ (a) and 1200 $\times$ (b) in BSE mode.

Based on the chemical analysis described above, the total elements were determined, while with the SEM together with the EDS probe, it was possible to analyze very small crystalline zones and the amorphous areas to assess the possibility of alkaline activation of the materials.

The semi-quantitative chemical analysis performed with EDS is reported in Table 3.

Table 3. EDS analysis of crystalline and/or amorphous areas in pumice and lapillus samples.

Average Chemical Composition (EDS)	Lapillus (Crystalline Zone)	Pumice (Crystalline Zone)	Pumice (Amorphous Zone)
O	53.9%	52.6%	61.7%
Si	19.8%	21.5%	16.4%
Al	8.9%	9.4%	6.5%
Fe	5.8%	3.9%	2.7%
K	2.6%	3.7%	0.3%
Na	2.6%	2.8%	Traces
Mg	1.3%	1.6%	4.8%
Ti	0.5%	0.5%	0.4%
Ca	-	4.5%	7.2%
P	0.3%	-	-

3.2. Thermal Characterization

3.2.1. Thermogravimetric and Differential Thermal Analysis (TGA/DTA)

The thermal investigation was conducted on all the raw materials with the exception of zeolitic tuff, as it could not be easily subjected to thermal processes.

The following figures describe the thermograms with their peaks (endothermic or exothermic) and the weight variation of the material under study. The red curves describe the TG while blue curves describe the DTA.

Figure 12 shows the results of the analysis conducted on lapillus.

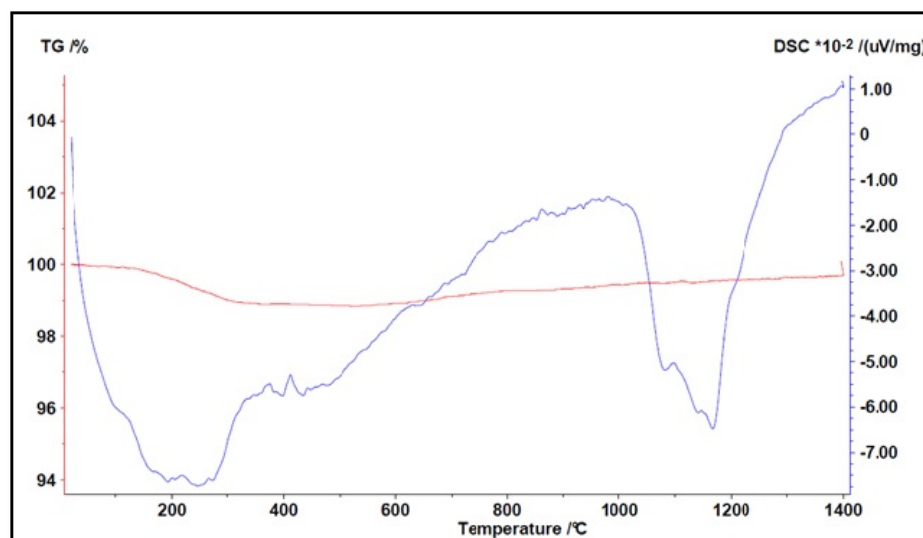


Figure 12. Simultaneous TGA/DTA analysis of lapillus (↑ exo peaks, ↓ endo peaks).

The red curve showed a material with a low LOI (loss on ignition) of around 1%, indicating its high thermal stability; the sample has a low interstitial water content.

Three main events can be described from the blue curve:

- Up to a temperature of about 200 °C, there was a loss of moisture resulting in a loss of about 0.5% of the initial weight;
- Between 500 °C and 1000 °C, substantial stability of the material was noted during heating;

- Around 1200 °C, there was an endothermic peak due to the melting of the crystalline lattice constituting the material, which as confirmed by the mineralogical analysis data, has an exclusively crystalline microstructure (approx. 87%).

The behavior of pumice with increasing temperature can be seen in Figure 13.

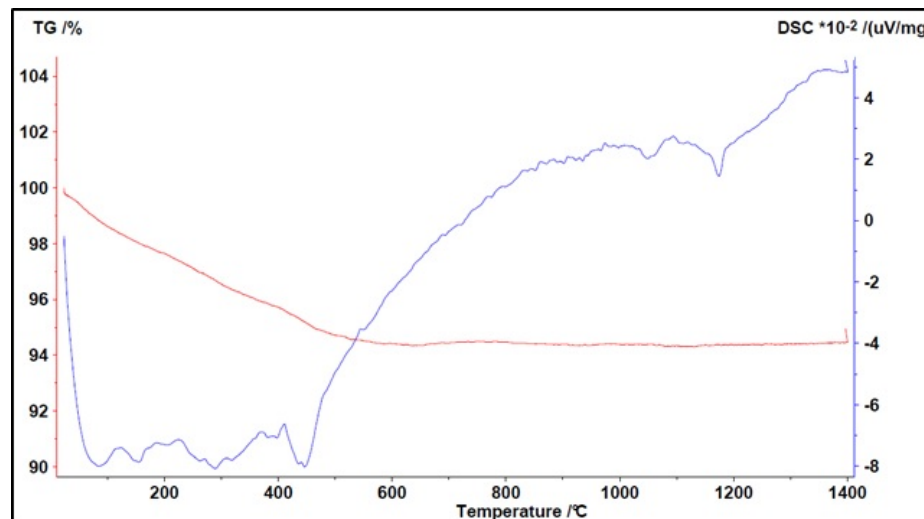


Figure 13. Simultaneous TGA/DTA analysis of pumice (↑ exo peaks, ↓ endo peaks).

Compared with lapillus, pumice showed a greater weight reduction. A LOI of around 6% was observed in the TG analysis, which is in agreement with other authors [30,31], with the greatest weight loss at temperatures below 500 °C due to the removal of moisture as well as OH species linked to metal oxides. With reference to DTA, an endothermic event was observed around 450 °C, which could be traced back to the dihydroxylation of the muscovite clay. The material remained stable up to around 1000 °C and then underwent melting of different crystalline phases at temperatures of around 1050 °C and 1200 °C, resulting in two separate peaks.

The behavior of Arlena sand can be observed in Figure 14.

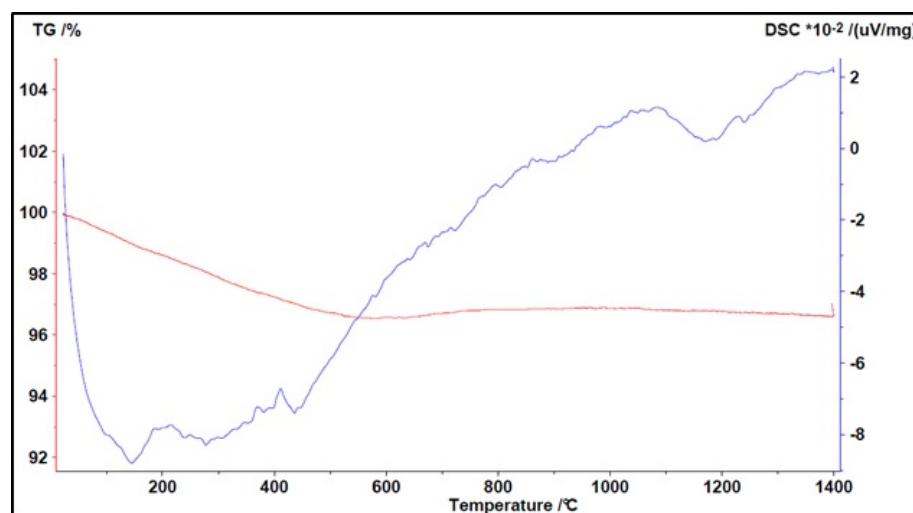


Figure 14. Simultaneous TGA/DTA analysis of Arlena sand (↑ exo peaks, ↓ endo peaks).

The blue curve showed a peak at a temperature below 200 °C, which is attributable to the loss of moisture, and a peak at around 1160 °C due to the melting of the crystalline phases.

The red curve showed a total weight loss of 8%, although this phenomenon mainly occurred at $T < 400$ °C.

The behavior of Tessennano sand can be observed in Figure 15.

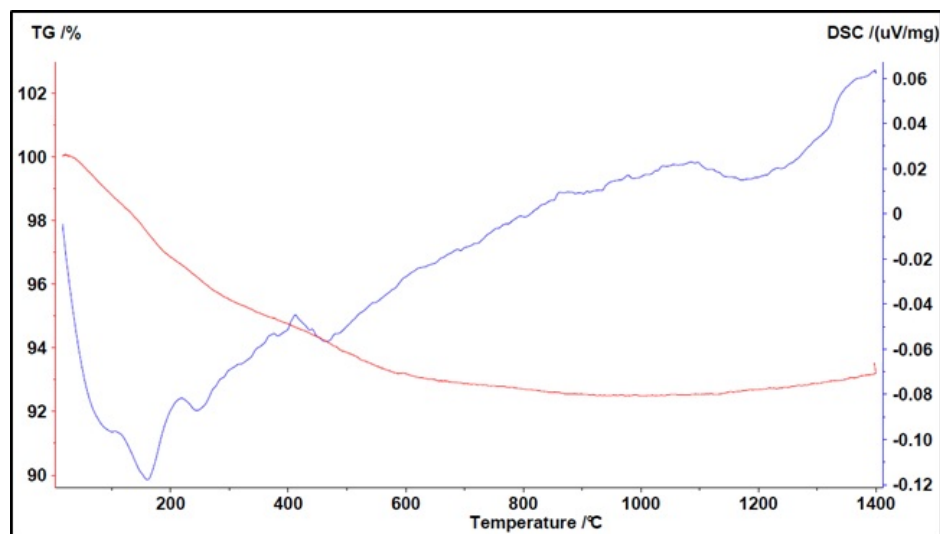


Figure 15. Simultaneous TGA/DTA analysis of Tessennano sand (↑ exo peaks, ↓ endo peaks).

The TG showed a weight loss of about 8%, which occurred mainly at $T < 600$ °C.

The DTA allowed three main events to be described:

- Up to a temperature of about 200 °C, there was a loss of moisture;
- Between 400 °C and 500 °C, there was a loss of reticular water most probably related to biotite;
- Around 1200 °C, there was an endothermic peak due to the melting of the crystalline phases.

3.2.2. Hot Stage Microscopy

Hot stage microscopy allowed the characteristic temperatures of the samples to be determined (Table 4). This knowledge is helpful in determining the optimum ranges of manufacturing conditions for ceramic processes.

Table 4. Characteristic temperatures.

Samples	T Sintering (°C)	T Softening (°C)	T Sphere (°C)	T Semi-Sphere (°C)	T Melting (°C)
Lapillus	1132	1181	n.a.	n.a.	1224
Pumice	972	1004	n.a.	1274	1319
Zeolitic tuff	949	1144	n.a.	1245	1314
Arlena sand	970	1210	n.a.	1298	1341
Tessennano sand	1033	1227	n.a.	1307	1347

The HSM provides information about the characteristic temperatures at which changes occur:

- Sintering temperature: the temperature at which the sample is reduced by about 5% and the sintering process of the grains begins;
- Softening temperature: the temperature at which the sample takes on a plastic character, and both the upper profile and the edges tend to round off;
- Sphere temperature: the temperature at which the height and width have the same magnitude, resulting in a spherical shape;
- Semi-sphere temperature: the temperature at which the width of the sample reaches dimensions twice as large as the height;
- Melting temperature: the temperature at which the width of the sample is three times its height.

4. Discussion

In this study, the characterisation of the materials, which are almost all extraction scraps, was driven by the need to investigate their alternative uses.

Lapillus, pumice and the two types of debris (Arlena sand and Tessennano sand) were the extraction scraps for which the particle size curve was analyzed. No scraps are produced in the extraction of zeolitic tuff. Zeolitic tuff can be exploited for various uses. If it is very fine ($<250\text{ }\mu\text{m}$), it can be used for foliar treatments in organic farming and for gas purification possibly after a micronization process [32–34], while if it is coarse ($>1\text{ mm}$), it is used for wastewater treatment due to its capacity for adsorbing contaminant [35] or as a soil conditioner for improving physical and chemical soil properties [36].

The chemical and mineralogical analyses showed that all the materials are aluminosilicates. The two volcanic debris were very similar to each other in both chemical and mineralogical composition and to pumice because they are scraps coming from the extraction operations of pumice. They also show a high fraction of vitreous phase (around 60–70%) due to their volcanic origin. Lapillus and pumice, although both materials originating from explosive type eruptions from magmas of acid composition, show differences that are probably due to the different rates of solidification. Lapillus has much higher amounts of Fe and Ca, resulting in its darker color, while pumice has higher amounts of Na and K. Both materials were observed to contain amounts of Si and Al comparable to the values reported in the literature [9]. Pumice presented the highest amount of amorphous phase (around 80%), and compared with lapillus, had higher alkaline oxides ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) and lower alkaline-earth oxides ($\text{CaO} + \text{MgO}$) contents, with a corresponding melting role in high temperature applications. This is also supported by lower sintering and softening temperatures detected by hot stage microscopy.

The pH and specific conductivity were assessed for all volcanic products in stirred mode to understand the tendency of the materials to release ions in solution. The pH values varied between 6 and 7.6, and being within the neutrality, the products are suitable for agronomic purposes [37]. Concerning electrical conductivity, lapillus was the most stable in terms of ions released in solution, compared with the other volcanic products. This behavior can be attributed to the lower amount of potassium (3.66%), a highly soluble ion, in lapillus. Pumice released more ions in water and showed an increasing tendency related to the higher amount of K^+ ions (8.55%). The two sands showed almost similar values, especially under stirring conditions.

As far as true density is concerned, the reported values allow some conclusions to be drawn: The higher values for lapillus can be related to the presence of higher density crystalline phases such as anorthite ($2500\text{--}2800\text{ Kg/m}^3$) and hematite ($5120\text{--}5300\text{ Kg/m}^3$). The values for pumice can be related to the presence of crystalline phases such as sanidine ($2550\text{--}2630\text{ Kg/m}^3$). The sand values are mainly attributable to the density values of quartz (2650 Kg/m^3) and sanidine, and the lower values of zeolitic tuff are attributable to the presence of chabazite.

The bulk density values presented demonstrate the lightness of these materials. For this reason, they can be exploited in the formulation of lightweight aggregates. In particular, the lower bulk density value in pumice results in better behavior in lightweight aggregates, as already observed by Righi et al. [7].

SEM analysis was conducted on pumice and lapillus only. The SEM analysis agrees with the mineralogical analysis, confirming that lapillus is more crystalline while pumice is more amorphous, as already reported by Pinarci et al. [38]. Given the aluminosilicate nature of both these materials with a significant amorphous fraction, they have been used by other researchers as precursors to obtain geopolymers [10,17]. In the literature, no uses of lapillus are found. However, Szabo et al. produced geopolymers starting from mechanically activated pumice [39], and Ulusu et al. produced pozzolanic cement with a high volume of pumice [40].

Furthermore, due to their amorphous silica content these products could be used also as precursors for obtaining activating solutions. Indeed, other studies in the literature

have successfully exploited other similar materials, such as diatomaceous earth, to activate aluminosilicate raw materials. Diatomite is a sedimentary rock with a high amorphous silica content similar to the volcanic debris discussed here, and it is used as silica source for obtaining waterglass to activate aluminosilicate precursors [41]. The EDS analysis confirmed the mineralogical characterization showing that the crystalline part of pumice is enriched in Si, Al and K, corresponding to the sanidine crystalline phase, while in the amorphous fraction, alkaline earth elements (Ca and Mg) are concentrated together with Si and Al. Furthermore, the EDS analysis showed an Si/Al ratio of 2.29 for the crystalline fraction and a ratio of 2.52 for the amorphous fraction. The latter is particularly reactive in an alkaline environment. The Si/Al ratio is very important in the design of a geopolymer because it influences the physical properties of the material: if it is between 2 and 3, a structure with rigid bonds is obtained and the material is comparable to cements and ceramics [42,43]. The importance of amorphism in an aluminosilicate precursor for geopolymers is confirmed in the literature [44]. Finally, thermal analyses were conducted to also assess the behavior of materials when subjected to firing, as in the case of lightweight aggregate or ceramic tile production.

It can be concluded that, with the exception of zeolitic tuff, these materials could be exploited in aluminosilicate matrices as substitutes for virgin raw materials, both for cold and hot consolidation. This is important since, given the current geopolitical situation, some raw materials are difficult to obtain, and these materials could replace, for example, feldspars or fluxes in ceramic pastes and glaze compositions, clays in lightweight aggregates (LAWs) or metakaolin in geopolymers.

In a previous study [17], the authors used lapillus and pumice to completely replace the red clay in LWAs compositions, using spent coffee ground (SCG) for pore-forming, and employing the same optimized ratio for clay (volcanic minerals/porous agent 85/15 wt%/wt%). Two compositions were prepared: one with only pumice + SCG (85 wt% + 15 wt%), and the other with a mix of equal parts of pumice and lapillus + SCG (85 wt% + 15 wt%). The lapillus-based compositions were not fit for purpose. The spherical samples were fired at 1000 °C for 1 h in an electrical kiln that was already hot in order to simulate the thermal shock that the aggregates undergo during industrial processes, which however, generally occur at higher temperatures (from 1200 to 1400 °C). The preliminary results obtained highlighted that the tailored compositions complied with the standard regarding the required particle density being lower than 2000 Kg/m³ (UNI EN 13055:2016 rule). In addition, they had a total porosity of around 60%, which is similar to values found in commercial products such as Arlita Leca L. These physical features suggest their application as a draining medium on green roofs. In particular, low density is an important factor when choosing the drainage components in the layers. In Figure 16, it is interesting to note that the substitution of clay by volcanic scraps has a positive effect on the density. This valorization of volcanic scraps represents a valuable way to manufacture light-weight aggregates for agronomic purposes on green roofs. This could be significant considering the advantages of green roofs for reducing the urban heat island effect, the energy consumption of buildings, air and noise pollution, as well as improving the quality and regulation of rainwater, and protecting biodiversity.

Pumice and lapillus could also be used for the production of cement mortars or lightened concretes, both as supplementary cementitious materials, i.e., by substituting Portland Cement, or by substituting commercial aggregates. In addition, Arlena and Tessennano sands could replace commercial sands in the construction industry. Preliminary laboratory tests have shown the possibility of incorporating them as an inert fraction in a geopolymer mortar, which by their mechanical performance (their measured compressive strength was about 2.6 N/mm²) fall within the class of performance-guaranteed mortars according to UNI EN 998-2.

The two sands could be exploited as an alternative inorganic component for the formulation of alternative substrates to peat. Further, both sands and zeolitic tuff, could be used in the design of technical green areas.

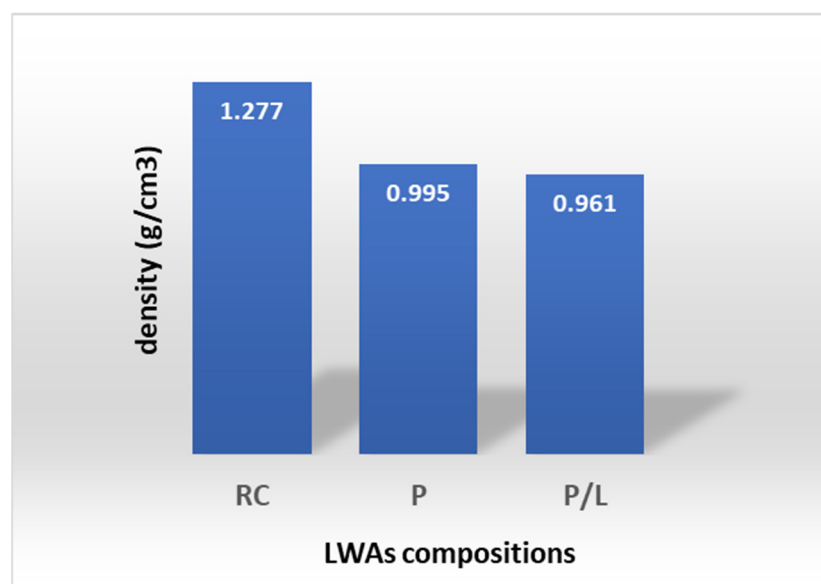


Figure 16. Particle density of the composition analyzed (RC only red clay; P: pumice; P/L: pumice lapillus).

Zeolitic tuff and pumice could be used for flue gas treatment and water purification. In particular, regarding the use of zeolitic tuff for gas purification, a previous study examined the design of a plant with a process that uses natural chabazite-based zeolitic tuff powder to purify industrial gases from harmful organic substances. The purification of the gas takes place thanks to the open structures with high surface areas typical of zeolitic tuff. This plant could replace existing combustion-type plants, which have the problem of not being able to remove particularly low concentrations of pollutants. It could also replace activated carbon filters, whose efficiency is conditioned by a series of parameters such as the molecular weight and concentration of pollutants, temperature, humidity, pressure [45].

The potential of these materials is very high. The latest studies performed by the authors focus on the replacement of foreign feldspar by Italian pumice or lapillus scraps as fluxing agents in the production of ceramic bodies. They are also able to confer color, thereby reducing the use of dye pigments, thanks to chromophore oxides present within the pumice and lapillus.

In the future, it would be interesting to compare the behavior of these volcanic rocks with sedimentary rocks with similar properties. For instance, diatomaceous earths are silicate raw materials with low density, high porosity, good absorbability, and other characteristics similar to pumice or zeolitic tuff. However, the different origin and texture could lead to different reactivity. The vesicular rough-textured nature of volcanic glass, which may or may not contain crystals of pumice, should give it greater responsiveness and efficiency in certain contexts compared with diatomaceous earths constituted by fossilized diatom skeletons. Some authors have already experimented with the possibility of obtaining porous materials for horticulture purposes with long-term nutrient effect based on a vitrifying agent in the form of pumice scraps [7].

Moreover, in the field of abatement of pollutants (in particular, pollutants of organic nature, such as C_6H_6) in industrial gaseous streams, the efficiency shown by zeolitic tuff, thanks to its open structures with high surface areas and ionic exchange capability, is practically unique and is subject to a patent by the authors [45].

5. Conclusions

In this paper, we analyze and report on the main work performed on volcanic rocks and materials derived from them, with the aim to create a database from which industry can take inspiration for enhancing circularity by using these raw materials in production cycles.

From the results presented in this paper we conclude that:

- Due to the lightness of the volcanic products, they can be used in the design and preparation of lightweight aggregates useful for agronomic purposes or in the construction field;
- Due to their aluminosilicate nature together with the presence of an amorphous fraction, pumice and lapillus can play the role of precursor for geopolymer preparation;
- Zeolitic tuff can be exploited for flue gas treatment, which is made possible by its porous nature and open structures with high surface areas;
- Due to the presence of feldspathic phase (sanidine), volcanic debris can be used in tile production as the melting component. Thanks to its pozzolanic activity and calcium content it could also be used in binders as supplementary cementitious material or as aggregate.

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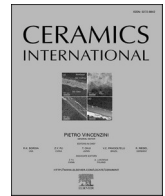
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Pumice and lapillus scraps: New national environmental-friendly chance for the production of ceramic tiles

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ABSTRACT

Italian pumice and volcanic lapillus scraps have been used in different percentages as alternative raw materials to foreign feldspars in porcelain stoneware mixtures. The aim of this work was to create naturally colored support to limit the use of artificial dyes while maintaining the technical properties of the reference product. For this purpose, the significant presence of chromophores (Fe and Ti in particular) in by-products from extraction of Italian volcanic pumice and lapillus was exploited. The work was carried out in collaboration with a company: the products were made on a laboratory scale and then they were glazed and fired within the industrial production cycle (48 min, 1210 °C).

The resulting slip and the fired samples were characterized by measuring the efflux time, density, linear shrinkage, water absorption and tensile strength to evaluate the technological performance. In addition, thermogravimetric analysis (TG), differential thermal analysis (DTA), and optical and mechanical dilatometry were performed to study the thermal behavior of the formulations.

The obtained products could be classified as porcelain stoneware and belong to the B1a group (WA 0.5%, B.S. >35 MPa) in accordance with UNI EN 14411 ISO 13006.

1. Introduction

Italy ranks among the top seven ceramic tile producers in the world [1], and the Italian ceramic tile production in 2022 (preliminary) was found to be about 448 million m² [2] keeping production stable compared to the previous year. The World of ceramic tile production in 2021 was found to be about 18 billion m² with an increase of about 7% compared to 2020 [3].

In recent years, the ceramic industry has been challenged by first the pandemic, which caused a forced stop in production for a period, and later due to the political situation, which created problems in the supply chain of raw materials as well as an uncontrolled increase in natural gas and electricity prices. The ceramics industry is a highly energy consume industry and has also been faced with major challenges such as achieving the sustainable development goals imposed by the 2030 Agenda [4]. It must be considered that the production cycle of Italian ceramics already appears to be designed following the circular economy issues, indeed almost all production and purification waste is fed back

into the production cycle, about a quarter of raw materials travel by train, 97% of factories reuse process water, and about half of the energy used in production comes from cogeneration or renewable sources [5]. The increase in tile production, however, has led to the need to source an ever-increasing number of raw materials, and it must be considered that these turn out to be nonrenewable assets in the short term, therefore, may soon deplete. On the basis of the above considerations, rather than looking for new virgin raw materials, it is better to i) make the process more virtuous by trying to use scraps, waste or by-products from other production processes, and, in addition, ii) limit the environmental impacts caused by long-distance transportation by preferring local rather than foreign raw materials. The literature related to studies on ceramic substrates is numerous, and there are several researches based on the addition or replacement of several types of waste or refuse within ceramic mixtures for the production of porcelain stoneware. Conte et al. studied the technological behavior resulting from high percentages of flux replacement with different types of glass scraps [6] while Gualtieri et al. evaluated the inclusion of high percentages of borosilicate glass

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scraps in stoneware tiles fired at low temperature [7]. Some authors have evaluated the embedding of sodium-calcium glass scrap within the ceramic slurry [8,9] while the authors in the past have focused their attention on the reuse of glass from the disposal of cathode ray tubes [10]. The inclusion of glass scrap is a suitable option but only in small percentages because the densification process starts at lower temperatures than the reference temperatures and at high replacement rates leads to lower sintering efficiency with swelling effects [11]. The addition of these types of wastes in ceramic slurries could lead not only to a substitution of virgin raw materials but also to a reduction in firing temperature [7,8].

There are also feasibility studies in the literature related to replacing fluxes with quarry dust from zeolitic rocks, used for their fusibility, modest hardness and low cost [12] and blast furnace slag [13]. Other studies use scraps or wastes such as incinerator bottom ash and fly ash [14–16], foundry sand [17,18], eggshells to replace limestone [19], and composite materials from industrial plastic waste and recycled nylon fibers to improve the performance of floor tiles [20].

The objective of the present work was to replace foreign feldspars, mainly Turkish, within a porcelain stoneware production mixture with scraps that derive from the mining and processing operations of Italian volcanic rocks and that have limited commercialization because they are very fine: pumice and lapillus. Pumice and volcanic lapillus are aluminosilicate materials rich in alkaline earth metals that contribute to the fusibility of the system and rich in iron and titanium (3.94% and 0.54% in pumice and 9.15% and 1.08% in lapillus, respectively). Iron and titanium are chromophores, normally it is preferred that their sum is very low to obtain a white porcelain stoneware support (<1.5%). In our case, the percentage of these metals turned out to be very high, so we opted for obtaining a naturally colored support in brown tones in the case of the pumice-based mixture, and in grey/black tones in the mixture lapillus-based. Such a choice allowed the use of local by-products and permitted the reduction of the quantities of artificial pigments used for mass coloring of white supports. There are studies in the literature on the use of pumice rock as, for example, an alternative fluxing agent in the composition of transparent glazes for roof tiles [21], as a pegmatite substitute for the production of wall tiles [22] and as a micronized raw material for obtaining sanitary glazes [23].

2. Materials and methods

2.1. Raw materials and samples preparation

Italian pumice and volcanic lapillus scraps, having a size smaller than 3 mm and from their mining and processing operations in quarries located in the Vulsini Volcanic District (around Lake Bolsena, Lazio, Italy), were supplied by Europomice srl. The scraps have the role of substituting the foreign feldspars within a porcelain stoneware body taken as a reference. Changes in the properties of these rocks as a function of temperature allowed them to be considered as fluxes [24]. In addition to volcanic rock scraps, sodium-potassium feldspar scraps from the mining and processing operations of rocks located in quarries present in northern Italy were used.

The clay component, useful for providing plasticity to the ceramic piece, is provided by clays, sourced from central-western Germany and northern Italy, and kaolin, sourced from central Italy.

Sands from Emilia-Romagna (Italy), sands from Sardinia (Italy) and raw and fired scraps from the production process were also included in the mixture.

Raw materials were included within the formulations in varying percentages, and the various mixtures were tailored by comparing the resulting chemical and mineralogical analysis with those of the mixture currently in production in the industrial plant. Chemical analyses were performed with an ARL PERFORM'X model sequential X-ray fluorescence (XRF) spectrometer. Mineralogical analyses were performed with an X-ray diffractometer, model X'PERT 3 POWDER PANALYTICAL using

the Rietveld method. The quantitative analysis of the crystalline phases was obtained by Rietveld refinements, using GSAS software, and were recalculated based on the absolute mass of the corundum originally added to the mixtures as an internal standard.

All raw materials were dried in an oven at $150\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ for 4–5 h to remove moisture. To obtain the samples, the raw materials were mixed with water at a ratio of 1:0.8 or 1:0.45, depending on the density sought, and a fluidizer to increase the workability of the mixture has been used. The obtained slip was then dried, ground, and humidified to 6%. After the powders were compacted with a hydraulic press at a pressure of 70–75 MPa to obtain specimens with a diameter of 50 mm for firing (industrial cycle: 48 min at $1210\text{ }^{\circ}\text{C}$) and specimens having dimensions of 50 mm × 100 mm were used for calculating flexural strength. The pressures applied are very high and do not correspond to those applied during production. These pressure values allow for water absorption values comparable to those that would be obtained by direct firing on industrial kiln rollers and not on a refractory plate (the firing mode used for the samples). The prepared formulations can be seen in Table 1; the abbreviations L and P indicate lapillus-based and pumice-based ceramic bodies, respectively. Concerning the reference sample, it contains a mix of two German clays, a mix of five Italian feldspars, and a mix of six Turkish feldspars (sodium and potash sodium) and other Italian components. The reference consists of 18 raw materials, both Italian and foreign, while the studied formulations are made with 8–10 raw materials of which only one is foreign (German clay).

2.2. Slip characterization: viscosity, density and residual fraction

The slip was placed inside a Ford cup with a 4-mm-diameter nozzle, and the time required to empty the cup was measured.

The density value was obtained according to Eq. (1), once the weight of the suspension contained in the pycnometer and that of the pycnometer itself were known:

$$d \text{ (Kg / cm}^3\text{)} = (tw - pw) / 1000 \quad (1)$$

where: d density, tw total weight (g) and pw is the pycnometer weight (g).

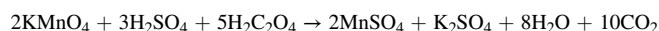
The residual fraction was obtained by passing the slip through a sieve having a mesh diameter of 63 μm and weighing the remaining solid mass on the sieve.

2.3. Unfired sample characterization

2.3.1. Permanganate oxidability

The presence of oxidizable substances within the mixture was evaluated through Kubel's method, an indirect titration method by which the ability of potassium permanganate to oxidize organic matter to CO_2 and H_2O in an acidic environment is analyzed when hot. This analysis makes it possible to assess the possible defects that could be encountered during cooking, such as, for example, the formation of black heart and subsequent swelling due to the presence of numerous oxidizable substances that would need more oxygenation to be flushed out [25].

The reaction that commands this phenomenon is as follows:



Potassium permanganate in the presence of sulfuric acid is reduced to manganous sulfate thus providing elemental oxygen for the oxidation of organic matter.

Inside a beaker containing 100 ml of double-distilled water were placed 1 g of ground sample, 5 ml of 1:3 H_2SO_4 solution and 10 ml of 0.01 M KMnO_4 , and the whole is then brought to a boil for about 10 min. After boiling, 10 ml of $\text{H}_2\text{C}_2\text{O}_4$ 0.01 M is placed inside the beaker and potassium permanganate is added until the color of the solution changes.

The result is expressed in mg/l of oxygen consumed, which is derived

Table 1

Batch prepared using P and L compared with the reference (only for the reference: a = mix of two German clays, b = mix of five Italian feldspars, c = mix of six Turkish feldspars).

	REFERENCE	L1	L2	L3	L4	P1	P2	P3	P4
German clay	35.4% ^a	34%	35%	35%	35%	33%	34%	35%	35%
Italian clay	3.8%	4%	3%	2%	2%	4%	3%	2%	2%
Italian kaolin	9.0%	8%	9%	8%	8%	6%	6%	8%	8%
Lapillus	–	13%	12%	12%	15%	–	–	–	–
Pumice	–	–	–	–	–	13%	15%	15%	16%
Italian feldspar	18.3% ^b	13%	23%	22%	19%	13%	15%	19%	17%
Turkish feldspars mix	24.1% ^c	–	–	–	–	–	–	–	–
Italian sand (Emilia-Romagna)	2.3%	–	–	3%	3%	6%	–	3%	5%
Italian sand (Sardinia)	2.3%	–	–	3%	–	–	–	–	–
Mix scraps	4.9%	15%	–	–	–	12%	12%	–	–
Chamotte	–	13%	18%	15%	18%	13%	15%	18%	17%

by multiplying the milliequivalents of permanganate consumed at the endpoint by the milliequivalent weight of oxygen and then dividing this product by the volume of sample used (0.1 L) [26].

2.3.2. Flexural strength

The flexural strength is a parameter used to evaluate the ability of the tile to resist static and dynamic loads when placed in service. The standard considers the tile as a beam, placed on two rollers spaced apart, while a force is applied in the center by a third roller. The breaking load is the weight that is borne before the specimen breaks. Measurement of this parameter on unfired ceramic specimens having dimensions 50 mm × 100 mm was carried out with a Gabbrielli Technology mini-CRC 2 Chrometer according to DIN 51030, UNI EN ISO 10545-4. Each measurement was performed on a minimum of 4 samples, and the value reported below is the average of the values of the individual samples. The instrument consists of a working base, which rests on the sensing element i.e., the electronic load cell, and houses the associated lower supports. The upper part is motorized and applies and controls the load during the working stroke (constant increment 1 N/mm²s). The breaking stress (S) is obtained by multiplying the breaking load *F*, i.e., the force applied at the centerline of the working surface, by the ratio *L/b* (roller distance/tile width). Once *F* is known, the breaking modulus (σ) can also be calculated according to Eq. (2):

$$S(N) = F \bullet L / b \quad (2a)$$

$$\sigma = 3FL / 2bh^2 \quad (2b)$$

The standard applies to all types of tiles and porcelain stoneware [27].

2.4. Fired sample characterization

2.4.1. Loss of ignition

Loss of ignition (LOI) was calculated according to Equation (3):

$$LOI(\%) = (w_i - w_f) / w_i \bullet 100 \quad (3)$$

where: *w_i* is the initial weight of the sample, *w_f* is the weight of the sample after firing.

2.4.2. Linear shrinkage

Linear shrinkage was calculated on fired specimens by measuring with a caliper the dimensional changes of the specimens in five different points to obtain an average value. The equation by which the parameter was calculated is as follows:

$$LS(\%) = (d_i - d_f) / d_i \bullet 100 \quad (4)$$

where: *d_i* is the initial diameter (50 mm) and *d_f* is the diameter of the sample after firing.

2.4.3. Vacuum water absorption

The fired samples were placed in a laboratory instrument (ISO-VACUUM 650, Gabbrielli Technology) to determine vacuum water absorption in ceramic tiles with fully automatic cycles. The vacuum test is carried out as follows: the tiles are placed in a special grid and fed into the tank (made of AISI - 304 stainless steel); then the cycle is started with the vacuum pump. When the required vacuum is reached and maintained, the pump stops. The tank, at this point, fills with demineralized water up to 50 mm above the maximum height of the tiles (adjustable level due to the presence of an electronic sensor). The vacuum regime is discharged, and the tiles remain immersed in the water for the time prescribed by the standard. In this way, apparent porosity, apparent relative density and water absorption can be determined. The instrument has been tested and set to perform ASTM C 373, ISO 10545-3, ISO 10545-12 4.2.6 standards. Once removed from the instrument, the samples were properly dried to remove excess surface water and weighed. The per cent water absorption (WA%) was calculated according to Eq. (5):

$$WA(\%) = (w_f - w_{pf}) / w_f \bullet 100 \quad (5)$$

where: *w_f* is the final weight, *w_{pf}* is the post-firing weight.

2.4.4. Thermal and thermomechanical characterization

A number of samples were subjected to thermal analysis and compared with the reference. The thermal characterization techniques used were thermogravimetric analysis (TG), differential thermal analysis (DTA), optical and mechanical dilatometry.

Differential thermal analysis allows evaluation of the behavior of powders as temperature increases, while thermogravimetric analysis allows the determination of the change in sample mass as a function of temperature again. This analysis was conducted on the mixtures to evaluate the firing behavior of the mixtures and to understand whether the firing temperatures could be lowered. TGA/DTA analyses were performed with a simultaneous thermal analyzer NETZSCH STA 429 (CD). The samples were ground to an impalpable powder (average particle diameter less than 20 μm), and the analysis was carried out at a heating rate of 10 °C/min.

The optical dilatometer is an instrument used to study the sintering of ceramic bodies and their thermal stability range while avoiding the risk of swelling by providing sample expansion (%) as a function of temperature as a result. Using optical technology, the best firing cycle can be determined without risking damage to the material. The measurement was performed with the Expert system ODHT-HSM solution mod. M3MD 1600/80, at a maximum temperature of 1280 °C and a heating rate of 10 °C/min, on solid samples prepared with a height of 15 mm, and with 5 × 5 mm edges. All samples were dried in an oven at 105 ± 5 °C overnight and stored in a desiccator before use. The samples tested were not fired.

The mechanical dilatometer was used to measure the thermal expansion of the specimens to obtain the Linear Thermal Expansion

Coefficient (α). The fired sample, having a length of 38–50 mm, was subjected to a constant negligible mechanical load and simultaneously to a controlled temperature/time program. Measurements were made with a MECHANICAL DILATOMETER, Netzsch Dilatometer 402 EP, with a heating rate of 5 °C/min setting a maximum temperature of 600 °C.

2.4.5. Colorimetry

In order to determine the effect of the addition of pumice or lapillus on aesthetic properties, fired samples were analyzed using a UV–vis spectrophotometer (SPECTROPHOTOMETER CM-2600d, KONIKA MINOLTA), which operates in the CIE L*a*b* color space, allowing the set of colors perceived by the human eye to be described.

This analysis was performed by comparison between the best fired samples and the reference. For each sample, five measurements were taken at different points of the surface to analyze any color variations, given by the ΔE parameter:

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} \quad (6)$$

If $\Delta E < 1$ two colors are no discriminable by convention.

3. Results and discussion

3.1. Characterization of mixtures

Chemical and mineralogical analyses were performed on the raw materials, not the mixtures, and were provided by the partner companies. The analyses on the mixtures reported below were not performed by spectroscopic analysis, but by calculating the percentages of the elements and crystalline phases based on the percentage of raw material in the mixture.

The formulations were selected on the basis of chemical and mineralogical similarity of the slurry samples to those of the reference. The comparison of the chemical and mineralogical analyses can be seen in Table 2 and Table 3, respectively.

By considering the comparison of chemical analyses, the slurries containing lapillus have similar percentages of silica and alumina to the reference with the exception of sample L2. The percentage of titanium oxide is comparable to the reference while iron oxide is almost two times that of the reference with the exception of sample L4 which has a higher percentage value, but in this case, it turns out to be an added value as it provides a darker coloration than the reference. CaO, MgO and K₂O are present in larger amounts than the reference while Na₂O is present in smaller amounts. As for the slurries pumice-based, the amounts of silica and alumina are found to be remarkably similar to those of the reference in all the formulations studied. The titanium oxide content is practically the same as the reference; therefore, it does not affect the coloration of the ceramic piece, while iron oxide has intermediate percentages between the reference and the lapillus-based slurry; in fact, it takes on an intermediate coloration visible in Fig. 1. Again CaO and K₂O are present in larger amounts while MgO and Na₂O vary and are present in smaller percentages.

An interesting ratio is that of silica/alumina, which turns out to be

identical to the reference in sample L4 and P2 and very similar in the other samples except L3.

Fig. 2 displays the different percentages of the oxides. It is possible to see a decrease in alkaline oxides and increase in alkaline-earth oxides. The ratio between alkali and alkaline-earth oxides drops significantly especially in P4. Alkaline-earth oxides help sintering by reducing temperature, so increasing their percentages improves the sintering process by affecting properties such as: shrinkage, water absorption and flexural strength.

Mineralogical analysis shows that samples L4, P3 and P4 have about the same quartz content compared to the reference, the percentage of kaolinite is found to be a bit lower for all samples except L1 where it increases slightly. The illite/mica content decreases in all samples and no sample except L3 has montmorillonite content. In general, the percentage of clay component decreases. The percentages of albite and plagioclase are found to be significantly lower than in the reference while the percentages of orthoclase increase in all samples.

The mineralogical analysis, unlike the chemical analysis, shows very different crystalline phases, and it can be seen that there are extremely high percentages of unreported phases in all the mixtures studied unlike the mixture taken as the reference.

The very high percentages in the samples containing pumice are mainly due to the percentage of amorphous fraction detected in the pumice (about 80%), while in the samples containing lapillus it is due not only to the amorphous fraction but also to the presence of hematite, which were not considered in the comparison with the reference.

3.2. Characterization of unfired samples

Fig. 3 and Table 4 show the values of the parameters analyzed on the slips and unfired sample.

The results of the measurements show quite similar values of efflux time working at low densities (1.4–1.5 kg/cm³) in the case of both lapillus-based and pumice-based samples. As the density increases, moving closer to the value of the reference, there is an increase in the efflux time, and this is due to higher viscosity of the slip as there is more solid loading and less water. If the efflux time value of the reference is compared with samples L4, P3 and P4, which have similar densities to the standard, it can be seen that its value is much lower in the sample containing lapillus than in the one containing pumice. The latter has efflux time values comparable to those of the standard while the lapillus-containing sample has lower values; this could allow, for the same fluidizer, a decrease in the amount of water required for slip preparation in favor of solid loading or use a lower amount of deflocculating agent.

The residual fraction was measured because it represents an important process parameter, as it allows an assessment of whether the grinding time of the mixture is adequate. The results reported for L4, P3 and P4 are very similar to those of the reference while the other samples presented much lower values. The difference can be attributed to the fact that the above samples were ground for 7 min while the remaining samples were ground for 9 min. It can be assumed that a grinding time of 9 min appears to be too long.

Regarding the presence of oxidizable substances in all samples, the

Table 2
Chemical analysis.

	Reference	L1	L2	L3	L4	P1	P2	P3	P4
SiO ₂	69.7	68.2	58.7	69.6	68.4	69.6	68.8	69.5	69.4
Al ₂ O ₃	17.8	17.8	14.5	16.7	17.5	17.4	17.9	17.5	17.4
Fe ₂ O ₃	1.2	2.3	2.1	2.2	2.4	1.6	1.7	1.7	1.7
TiO ₂	0.7	0.8	0.7	0.7	0.8	0.7	0.7	0.7	0.7
CaO	0.6	1.9	1.4	1.7	2.0	1.1	1.1	1.0	1.1
MgO	0.7	0.9	0.7	0.8	1.0	0.5	0.5	0.5	0.5
K ₂ O	2.2	2.6	2.5	2.9	2.8	3.3	3.4	3.5	3.6
Na ₂ O	3.4	1.7	0.9	1.5	1.5	1.7	1.7	1.5	1.5
Others	3.7	3.8	18.5	3.8	3.8	4.1	4.1	4.2	4.3

Table 3
Mineralogical analysis.

	Reference	L1	L2	L3	L4	P1	P2	P3	P4
Quartz	30.7	29.8	31.7	32.8	30.4	30.6	28.3	30.5	30.5
Kaolinite	15.6	16.1	15.0	14.6	14.6	15.0	14.9	14.6	14.6
Illite/Mica	11.8	10.5	8.4	8.4	8.4	10.1	10.3	8.7	8.8
Montmorillonite	0.3	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0
Albite	23.3	5.9	5.1	5.4	4.8	6.4	5.7	4.8	4.7
Orthoclase	5.6	8.0	9.3	10.1	9.1	7.3	7.4	7.8	7.5
Plagioclase	8.1	3.4	1.6	1.6	1.6	2.8	2.5	1.2	1.2
Other or not reported	4.7	26.4	28.9	27.0	31.3	27.7	30.8	32.5	32.7

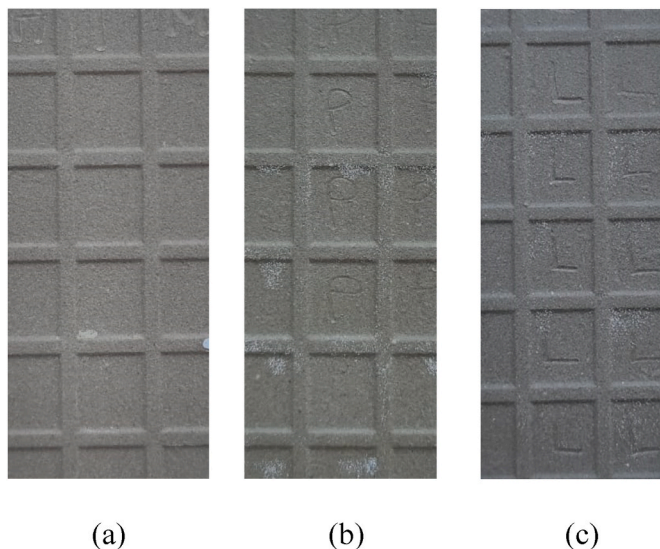


Fig. 1. Color variation in different mixtures: (a) is the reference, (b) is a pumice sample, and (c) is a lapillus sample.

values obtained were adequate and lower than the maximum limit imposed on the reference. Excessive presence of oxidizable substances could lead to the swelling of the ceramic piece due to the incomplete degassing of the organic products that burn turning into gas.

Flexural strength is measured because the tiles during transportation and processing are subjected to stresses, and the minimum reference value required is 35 MPa. The lowest strengths were recorded in samples L4, P2 and P3. L4 and P2 still presented acceptable values while P3 presented a value below the minimum required. One consideration that can be made is that, in general, the modulus of rupture tends to increase as the porosity decreases so the lower the water absorption, the lower the porosity and the higher the flexural strength of the tile. It should be considered that flexural strength, porosity, water absorption, and shrinkage during firing are parameters that could also depend on the number of alkaline-earth oxides as shown in some works in the literature, from which it was found that the extent of these properties depended precisely on the amount of CaO and MgO [28,29]. P3 presented a higher absorption value and consequently its flexural strength decreased. In the other samples, the value obtained is higher than the require minimum. The results obtained are consistent with the percentages of alkali-earth oxides in the various formulations, as shown in Fig. 2.

The optimized mixtures result to be L4 and P4, therefore the thermal characterization was performed on these formulation only. Figs. 3 and 4 describe the TG (red curve) and DTA (blue curve) with thermograms showing peaks, endothermic or exothermic, and weight change of the material under test.

Fig. 4 describes the behavior of the standard as temperature increases. The TG shows a not very high mass loss (4.06%), and the greatest loss occurs between 400 °C and 700 °C. From the DTA it can be

seen that:

- Up to about 150 °C, there is a loss of adsorbed water and crystallization;
- Between 370 °C and 479 °C, dihydroxylation of the clay component occurs;
- At about 570 °C the endothermic peak could be associated with the transformation of kaolinite to metakaolin;
- At 980 °C, on the other hand, an exothermic peak probably related to the crystallization of mullite, or alumina occurs;

around 1200 °C, an endothermic peak occurs due to the melting of the crystal lattice that makes up the material.

Fig. 5 describes the behavior of the sample containing lapillus. TG shows greater mass loss than the standard (6.14%), and the greatest loss occurs up to 600 °C. DTA shows that:

- Up to about 120 °C there is loss of adsorbed water and crystallization;
- Between 390 °C and 507.5 °C dihydroxylation of the clay component occurs;
- At around 571 °C the endothermic peak could be associated with the transformation of kaolinite to metakaolin;
- around 1150 °C an endothermic peak occurs due to the melting of the crystal lattice that makes up the material.

Comparing the lapillus-containing sample with the reference one, it can be stated that: the dihydroxylation of the clay component in the lapillus-based sample begins at higher temperatures; the peak at around 570 °C occurs at about the same temperature; the melting of the crystal lattice in L4 sample occurs at lower temperatures than in the reference.

Fig. 6 shows the thermal behavior of the mix containing pumice. TG shows a higher mass loss (6.78%) than the other two samples, and the highest loss occurs between 200 °C and 500 °C. DTA allows us to say that:

- Up to about 100 °C, there is a loss of adsorbed water and crystallization;
- Between 380 °C and 500 °C, dihydroxylation of the clay component occurs;
- At around 570 °C, the endothermic peak could be associated with the transformation of kaolinite to metakaolin;
- around 1150 °C, an endothermic peak occurs due to the melting of the crystal lattice that makes up the material.

When comparing the pumice-based mixture with the other two, it is possible to say that the sample has intermediate thermal characteristics between them. The dihydroxylation of the clay component in the pumice-containing sample begins at temperatures higher than the reference but lower than in the lapillus-based sample; the endothermic peak at about 570 °C occurs at about the same temperature for all samples while the melting of the crystal lattice in the L4 and P4 samples occurs at about similar temperatures but lower than the reference.

Optical dilatometry was performed on the standard and on L4 and P4 samples, and the results can be seen in Figs. 7–9, respectively. This

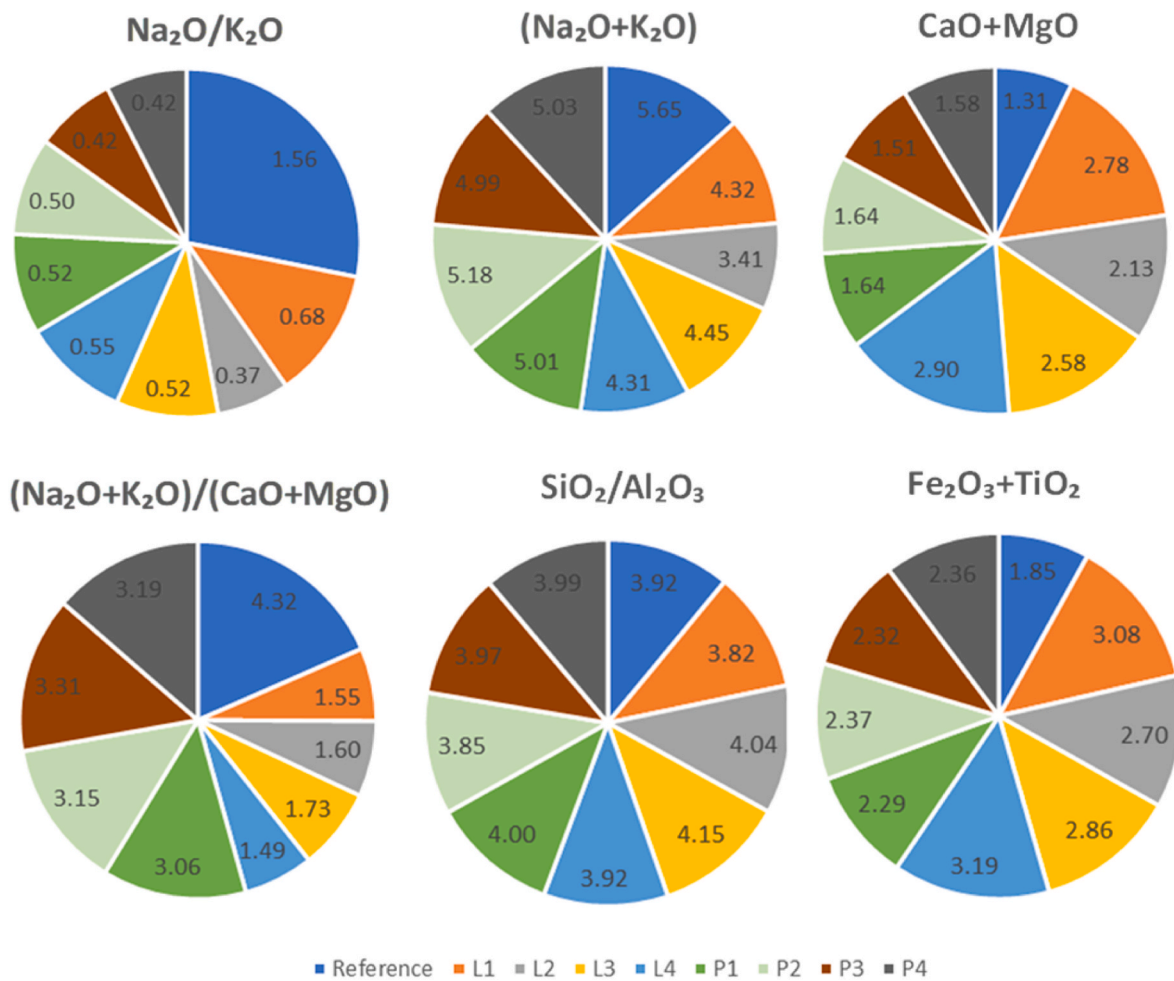


Fig. 2. Different percentages of oxides in the reference and formulations studied.

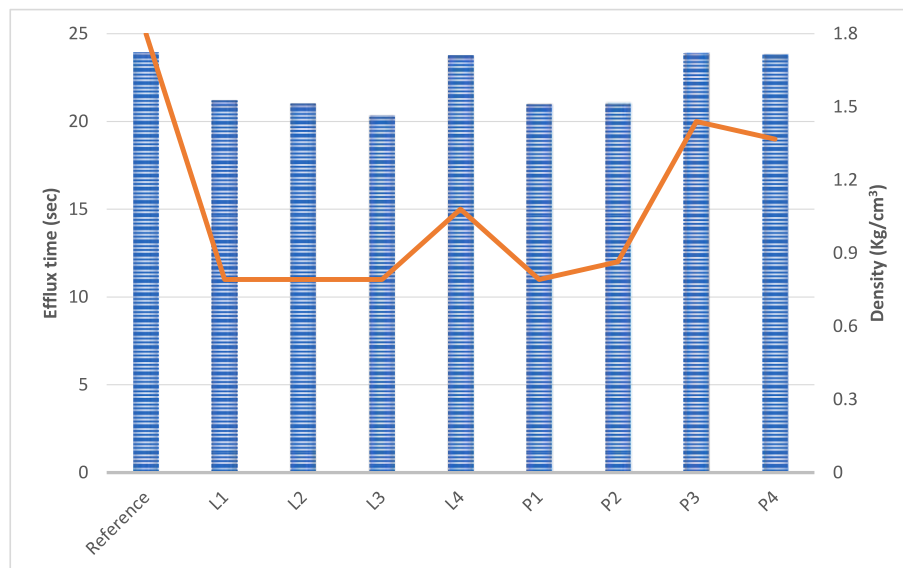


Fig. 3. Effect of efflux time variation as a function of density.

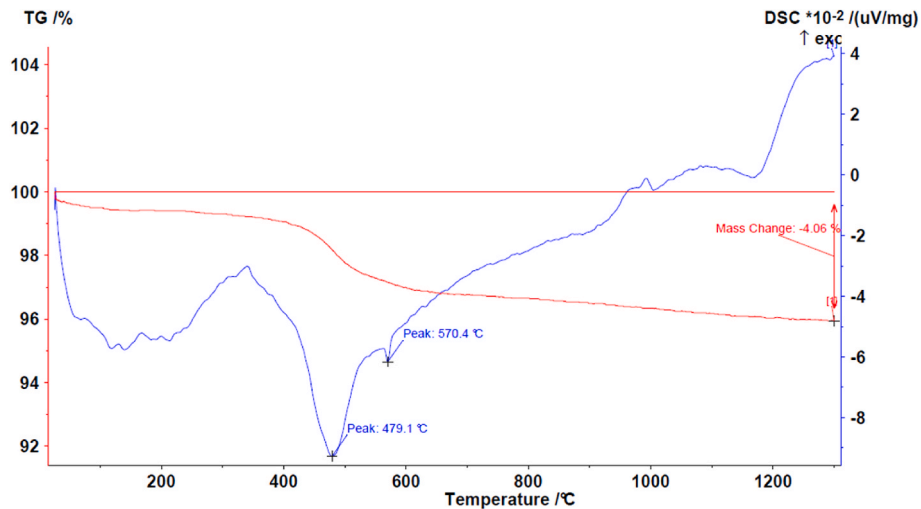
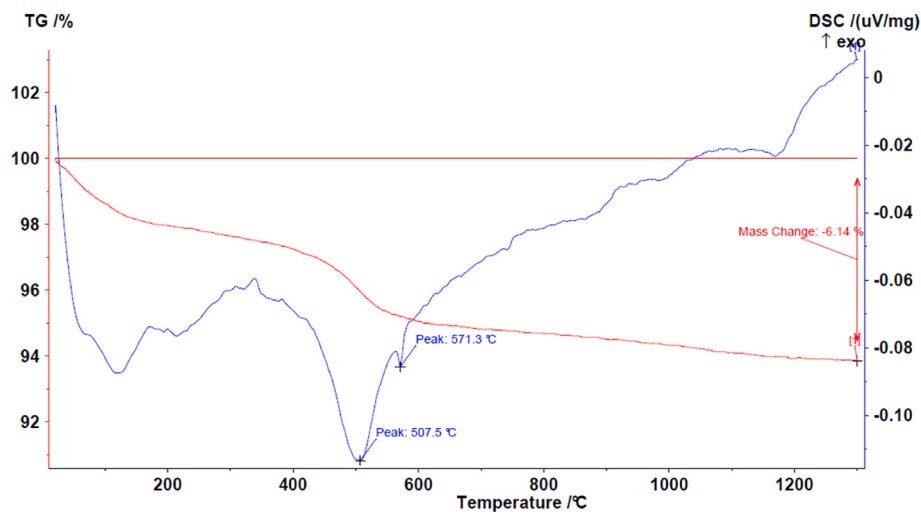
technique allows to estimate the temperatures corresponding to the beginning of sintering and the maximum sintering rate. There are two curves in each Figure: a blue curve that represents the sintering curve

and describes the behavior of the sample (expansion/shrinkage) as temperature increases and a dark pink curve that is derivative of the previous curve and allows the maximum sintering speed to be identified.

Table 4

Residual fraction, oxidizable substances and flexural strength.

	Reference	L1	L2	L3	L4	P1	P2	P3	P4
Residual fraction (g)	3.5–4.5	2.29 ± 0.05	1.94 ± 0.05	0.28 ± 0.05	3.75 ± 0.05	2.22 ± 0.05	1.82 ± 0.05	3.12 ± 0.05	3.72 ± 0.05
Oxidizable substances (mg/L)	<1	0.47 ± 0.05	0.63 ± 0.05	0.63 ± 0.05	0.63 ± 0.05	0.57 ± 0.05	0.60 ± 0.05	0.63 ± 0.05	0.63 ± 0.05
Flexural strength (MPa)	35–50	55.37 ± 0.5	42.52 ± 0.5	40.48 ± 0.5	37 ± 0.5	52.23 ± 0.5	35.54 ± 0.5	32 ± 0.5	45.63 ± 0.5

**Fig. 4.** TG/DSC reference body.**Fig. 5.** TG/DSC lapillus-based sample (L4).

Dilatometric analysis of the reference shows that there is an initial phase of loss of body water, structural water and organic matter up to about 500 °C, followed by an expansion phase at which sintering begins, and finally from about 1000 °C there is the vitrification phase with shrinkage of the ceramic piece. The ideal maximum firing temperature of the mixture is 1204 °C which corresponds to a shrinkage of about 3.2%.

Dilatometric analysis of the lapillus-based sample shows that there is again an initial phase of loss of body water, structure water and organic matter up to about 500 °C, followed by an expansion phase at which sintering begins, and finally from about 900 °C there is the sintering with viscous liquid phase where shrinkage of the ceramic pieces occur. The ideal maximum firing temperature of the mixture is 1205 °C which corresponds a shrinkage of about 3.9%.

The pumice-based sample exhibited loss of body water, structure

water and organic matter up to about 500 °C, a subsequent expansion phase (sintering), and from about 900 °C the sintering with viscous liquid phase permits the shrinkage of the ceramic piece. The ideal maximum firing temperature of the body is 1201 °C to which corresponds a shrinkage of about 4.1%.

The greatest shrinkage is evident in the pumice-based mixture. The ideal temperatures at the inflexion points are very similar to each other, but the pumice-containing formulation is slightly lower, probably due to the fact that as the maximum allowable temperature increases, the linear shrinkage of the ceramic piece increases.

3.3. Characterization of fired samples

Linear shrinkage, water absorption and loss of ignition were evaluated on the fired samples, and the values obtained can be seen in Fig. 10.

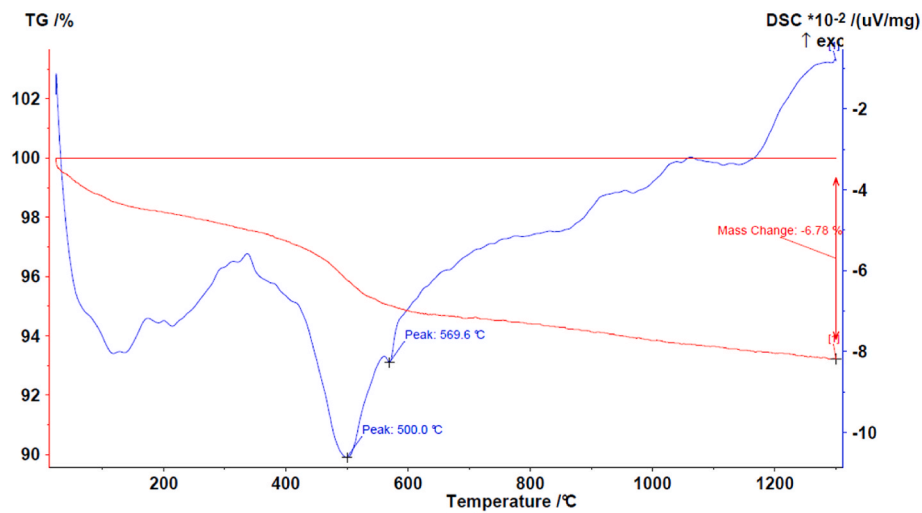


Fig. 6. TG/DSC pumice-based sample (P4).

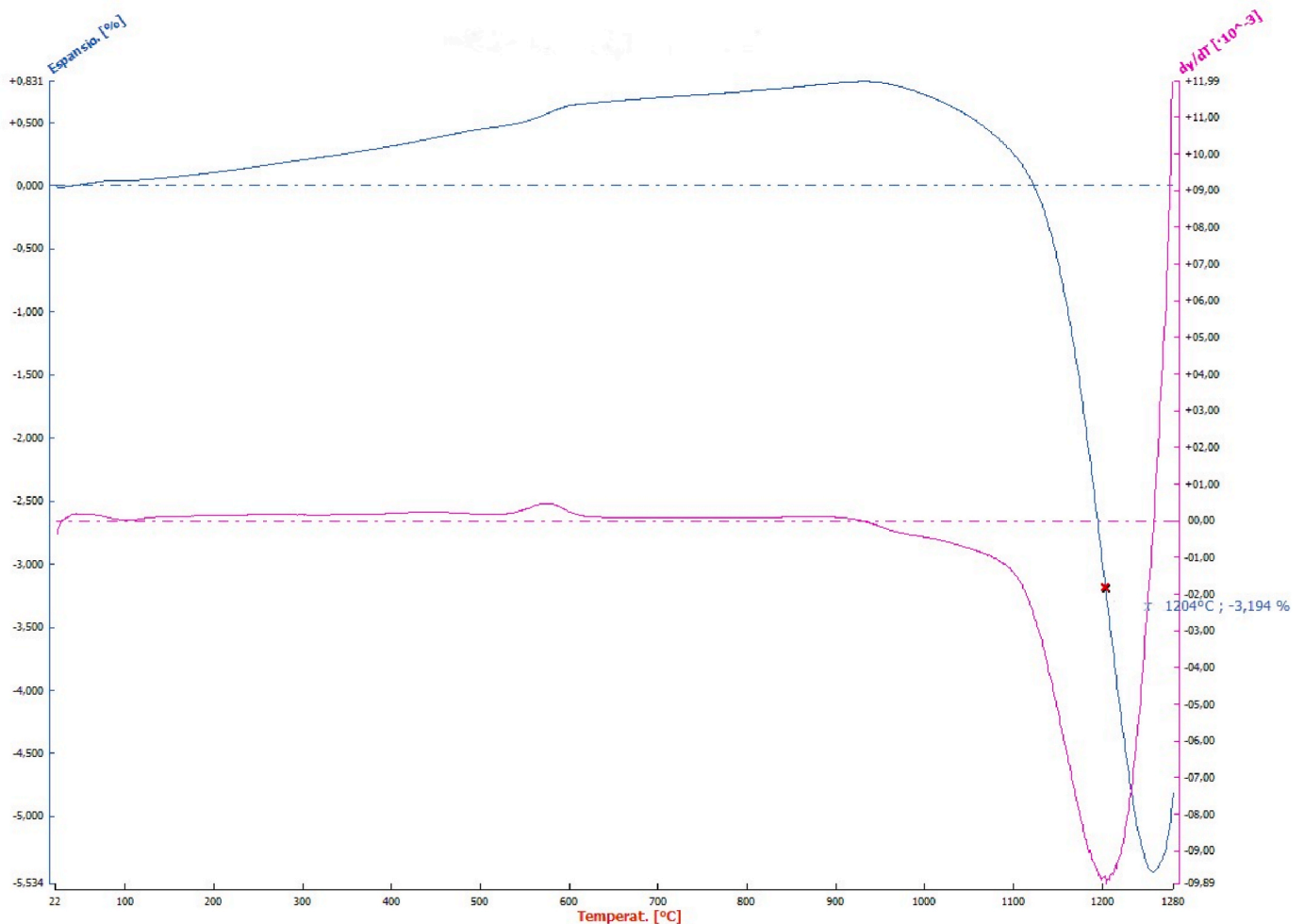


Fig. 7. Dilatometric analysis of reference.

The loss on ignition value obtained for the samples is similar to the standard one except for samples L1 (higher) and L2 (lower). The weight variation of the samples is monitored because it is necessary for the determination of the amount of organic and inorganic matter.

The standard presented a linear shrinkage value ranging from 4.6 to 4.9%. Sample L1 presented a very low shrinkage so it can be inferred

that it sintered less than the others at the same temperature. This could be attributed to the lower presence of Italian feldspar along with the presence of a mix of raw and fired ceramic scraps (chamotte) within the mixture. The other samples lapillus-containing presented values that were within or very close to the range of variation of the reference. As for the samples containing pumice in all cases, linear shrinkage took

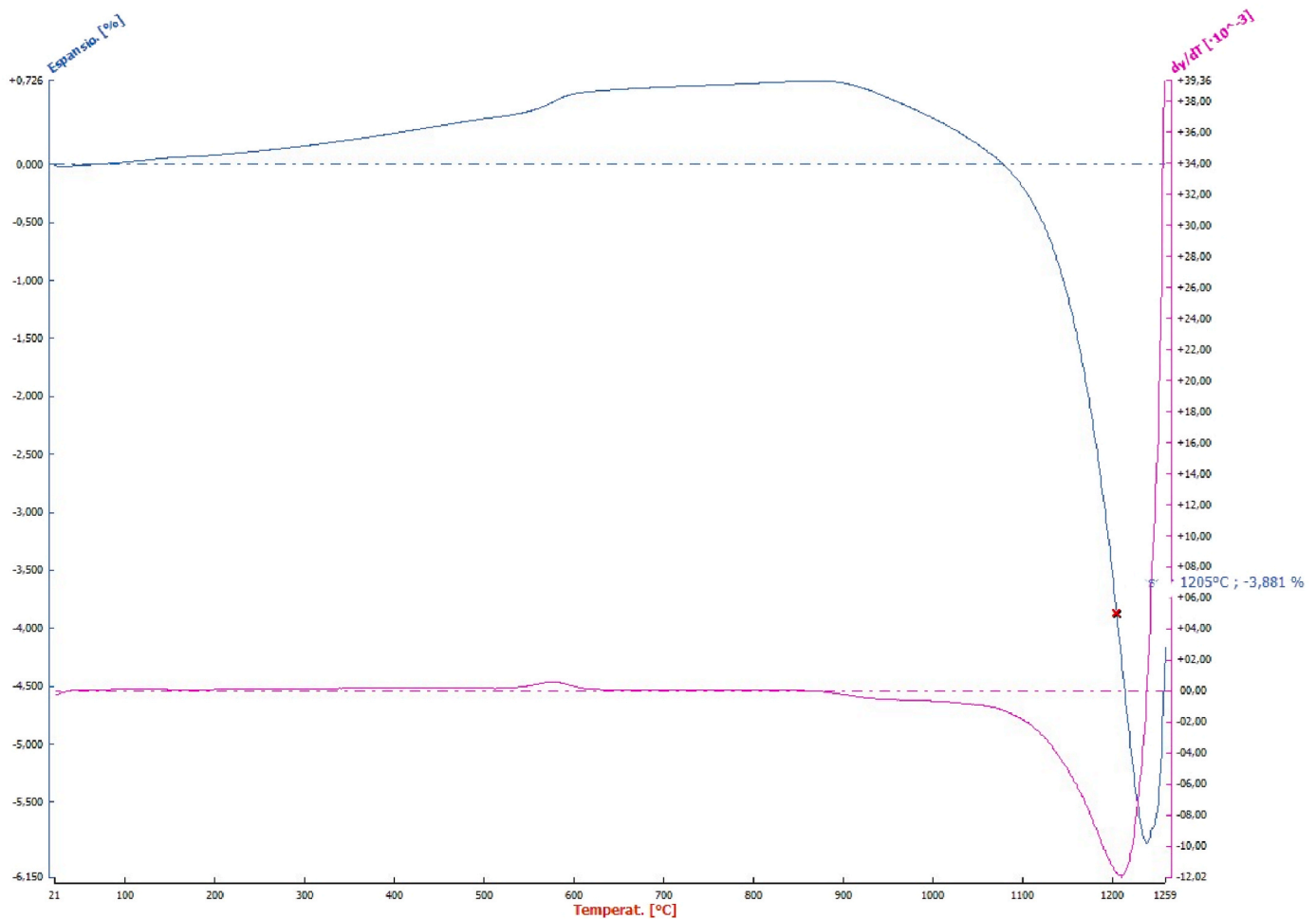


Fig. 8. Dilatometric analysis of lapillus-based sample.

higher values than the reference.

Water absorption is a normative parameter, and thanks to it, it is possible to make a classification of ceramic tiles according to their open porosity. International standards EN 14411 - ISO 13006 classify tiles according to the percentage of water absorption as follows:

- BIa: $WA (\%) \leq 0.5\%$;
- BIb-BIIa: $3\% < WA (\%) \leq 6\%$;
- BIIb: $6\% < WA (\%) \leq 10\%$;
- BIII: $WA (\%) > 10\%$

B indicates that the product was formed by pressing.

The reference is a porcelain stoneware tile that falls into class BIa (water absorption $< 0.5\%$). Based on the reported values, tiles can be obtained from all mixtures that fall in the same class as the standard except for the P3 mixture, which has a higher value. The water absorption was evaluated on unglazed samples so it can be deduced that the value could be further reduced, as the glaze could close the open porosity of the sample. It can be seen that samples L2 and L3 have a variation in the value of absorption, and this could be due to the inclusion of Italian sands in L3 leading to the decrease in the value of this parameter. Most of the samples, although unglazed, showed acceptable water absorption values, and this could be explained by the increased content of alkaline-earth oxides in the studied formulations (Fig. 2), in agreement with literature data [28,29].

Mechanical dilatometry was performed on the reference, L4 and P4 samples but also on the glaze and engobe used in the company to assess the dilatometric agreement of the mixtures studied with the latter. The

data obtained are shown in Table 5.

When glaze and mixtures containing clay are heated, they expand. As they cool, they shrink. The best situation is when the support shrinks a little more than the glaze; this keeps the glaze in slight compression. If the glaze shrinks more than the support, there is cracking creating small fracture lines ("cavillo" defect). If the glaze shrinks less than the support it is subjected to compression, which being too high causes it to peel off, especially at the edges, or the glaze clumps leaving surfaces of the support exposed [30].

The coefficients obtained show that there is a dilatometric agreement between glaze, engobe and samples L4 and P4.

Sample P4 shows values very close to those of the reference, while sample L4 shows values of the coefficient lower than the standard. Thus, it can be assumed that the studied compositions could be substituted for the reference without making ad hoc glazes or engobes for the new substrates in question.

Colorimetry was performed with the CIE $L^*a^*b^*$ system, most widely used in the ceramic industry. This method allows the color of tiles to be determined by measuring the three parameters L^* (brightness) from absolute white $L = 100$ to absolute black $L = 0$, a^* (red-green), b^* (yellow-blue) processed from the visible spectra. Table 6 shows the results obtained.

A decrease in L^* , a^* , b^* parameters was seen with the presence of pumice and lapillus in the composition. Comparison between the reference and the pumice-based sample showed that the latter was greener and darker. On the other hand, comparison between the reference sample and the lapillus-based sample shows that the presence of lapillus makes the color darker and closer to the blue zone.

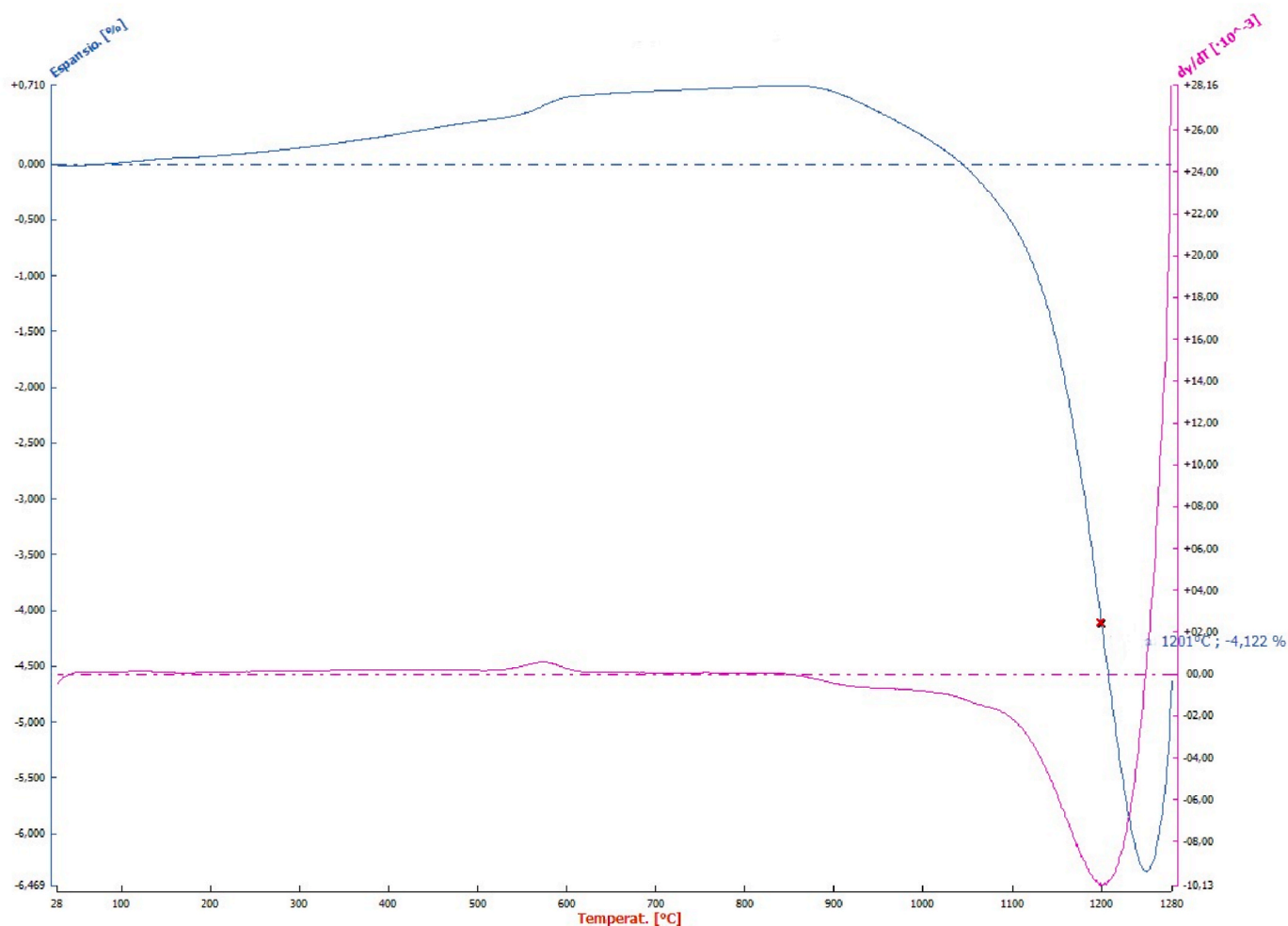


Fig. 9. Dilatometric analysis of pumice-based sample.

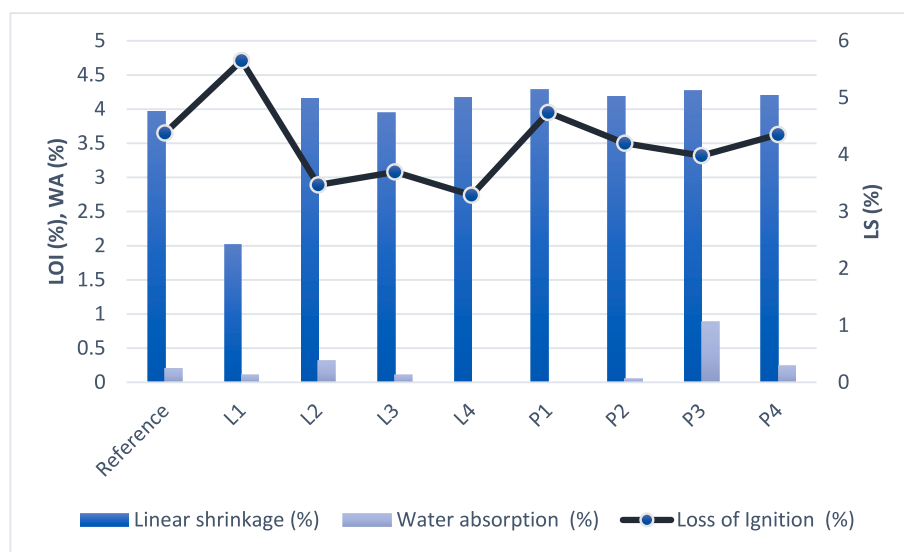


Fig. 10. Linear shrinkage (LS), water absorption (WA) and loss on ignition (LOI).

4. Conclusions

Ceramic bodies have been formulated by replacing foreign feldspars with about 40–50% waste and refuse, of which 10–16% is volcanic raw

material scraps. Pumice and lapillus have been successfully incorporated and used not only as fluxes but also as natural colorants. The mixtures studied have shown good mechanical properties, low absorption, acceptable linear shrinkage and good dilatometric concordance with

Table 5

CIELab values obtained for the best samples compared to the reference.

	L*	a*	b*	ΔE*
Reference	59.69	4.48	10.91	0
L4	48.73	1.34	5.42	12.66
P4	52.98	2.36	10.29	7.06

Table 6Linear thermal expansion coefficient (α).

α	α (100–400 °C)	α (200–400 °C)	α (200–500 °C)	α (100–500 °C)
Reference	8.52E-06	8.79E-06	9.09E-06	8.81E-06
Glaze	7.48E-06	7.64E-06	7.64E-06	7.52E-06
Engobe	8.03E-06	8.30E-06	8.64E-06	8.36E-06
L4	8.24E-06	8.52E-06	8.88E-06	8.58E-06
P4	8.49E-06	8.75E-06	9.09E-06	8.81E-06

glazes and engobes currently in use, without changing the current industrial production cycle. Comparing the obtained mixtures with the reference, the number of raw materials has been decreased from 18 to a maximum of 10, at least 4 of which are recycled; the environmental impacts related to the extraction of raw materials and transportation of materials from foreign countries are decreased with a corresponding easier logistic; the volumes of water required for the production of slip in the case of the lapillus-based mixture are reduced; and the use of artificial dyes is significantly lowered. A product thus obtained, therefore, is a good example of circular economy and sustainability.

Considering the promising results achieved in this research and to encourage industrial transferability, an environmental impact assessment is underway through the LCA procedure.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

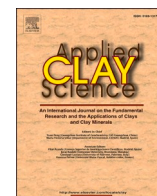
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Research Paper

Comparative study of technological behavior of German ball clay and Italian kaolinitic clay in unconventional porcelain stoneware body

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ABSTRACT

This work focused on obtaining a porcelain stoneware body containing only Italian raw materials. The starting mixtures differed in the feldspathic fraction, one pumice-based and one lapillus-based. German ball clay was gradually replaced by Italian kaolinitic clay. The influence of Italian kaolinitic clay on the technical and aesthetic properties of the final product was analyzed by comparing it with the references. The work was carried out in collaboration with a ceramic company which allowed the tile production process to be simulated in the laboratory and fired in an industrial kiln using the production cycle (48 min, 1210 °C). Ceramic bodies were characterized in order to evaluate technological performance by measuring efflux time and density of slip, flexural strength on green, linear shrinkage and water absorption in vacuum on fired samples. Mineralogical, microstructural (ESEM) and colorimetric analyses were also performed on the fired samples. Efflux time and density are processing parameters; these were in line with the reference in the lapillus-based bodies with kaolinitic clay replacement rates of 100%; in the case of the pumice-based bodies, they were considered acceptable only for replacements of 25%. The lapillus-based body showed a microstructure similar to that of porcelain stoneware. Vacuum water absorption values were better in lapillus-based formulations than in pumice-based formulations but showed higher linear shrinkage values for 100% replacements. According to UNI EN 14411 ISO 13006, some of the products obtained can be classified as porcelain stoneware (group B1a).

1. Introduction

The ceramic industry in recent years has been stressed firstly by the arrival of the pandemic, which caused a mandatory stop in production, and then by the conflict between Ukraine and Russia, which caused an increase in the prices of key raw materials such as methane gas and a drastic reduction in the export of Ukrainian clays. In addition to this, it must also be considered that ceramic industries must contribute to the achievement of the goals of the 2030 Agenda for Sustainable Development (United Nations, 2024). In this regard, the Italian ceramic tiles industry, in recent years, has worked to reduce its emissions and be increasingly sustainable. Indeed this sector has achieved high energy savings, significant reductions in water consumption thanks to the wastewater recycling (56% of water needs) and the reuse of almost all production wastes (De Ceglia, 2022; Confindustria Ceramica, 2024; Boschi et al., 2020; Settembre Blundo et al., 2019).

Due to the aforementioned events, the ceramic industries are always looking for new raw materials that can replace those already in use,

because both are difficult to find and the need to become independent from raw material imports is growing.

A porcelain stoneware body consists of a mixture of raw materials:

- plastic component provided by clays, in Italy the clays used come mainly from Ukraine and Germany;
- flux component, given by feldspars that come mainly from Turkey;
- inert component, provided by quartz sands and chamotte.

Numerous papers related to the study of formulations for stoneware or ceramic tiles bodies can be found in the literature. Analyzing the scientific works it is possible to find papers in which the technological properties of ceramic tiles were studied, where the clay fraction consisted of iron-rich clays: Italian red clay (Fantini et al., 2024) and Thai red clay (Nawaukaratharnant et al., 2022.) for the production of porcelain stoneware, lower clays rich in CaO and Fe₂O₃ for obtaining industrial prototypes of excellent quality with reduced firing temperature (Jiang et al., 2017). Mixtures for the production of porcelain stoneware

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based on Spanish kaolinitic clays after reducing, through physical processes, the impurities of iron compounds and organic matter (Barrachina et al., 2017) and based on Colombian kaolinitic clays, introducing different fluxes to increase the degree of sintering (Ramírez Calderón et al., 2019) have been studied. The behavior of Tunisian plastic clays has been compared with that of plastic clays commonly used in Italy for the production of porcelain stoneware (Molinari et al., 2023) but the behavior of white-baked plastic clays from central and eastern European regions has also been studied (Galos, 2011). Still, the use of serpentinite waste sludge from dunite quarries as raw materials in the ceramic industry has been evaluated (Díaz and Torrecillas, 2007), the replacement of part of the clay fraction with bentonites has been studied (Andreola et al., 2009), and the effect of hematitic iron ore and limestone additives on the stiffness of bentonite clay materials in porcelain stoneware paste has been investigated (Ismail et al., 2017).

The aim of this study was to obtain a body consisting only of Italian raw materials, starting from a porcelain stoneware body obtained in a previous work, where technological properties had been studied and evaluated. The starting porcelain stoneware bodies consisted of German ball clay, Italian kaolinite and Italian kaolinitic clay (the latter in a very low percentage) for the plastic component, mining and processing scraps of volcanic-sedimentary rocks (pumice rock or lapillus rock), Italian feldspar scraps for the flux component, and feldspathic sand and chamotte (from the same production cycle) for the inert component (Altimari et al., 2023). Italian kaolinitic clay gradually replaced German ball clay at 25%–50%–100%. The obtained products were compared by analyzing the main technological parameters to assess the differences due to substitution and any strengths or weaknesses.

2. Materials and Methods

2.1. Raw materials and samples preparation

Raw materials used in this work were: commercial ball clay from central-western Germany (Westerwald region, loc. Meudt), the deposits are of a fluvio-lacustrine environment (dating from the Eocene-Oligocene period) and result from the alteration and erosion of Devonian groves, shales and quartzites; commercial kaolinitic clay from northern Italy (Piedmont region, loc. Novara), the deposits are of a fluvio-lacustrine environment (dating from the Pliocene-Pleistocene); commercial kaolinite from central Italy (Lazio region), originating from kaolinitic deposits formed by hydrothermal alteration phenomena at Quaternary volcanites; sedimentary-rock scraps (pumice rock and lapillus rock) from central Italy, located between Viterbo and Grosseto (Barbieri et al., 2023); feldspar scraps from northern Italy (Piedmont region); feldspathic sand from northern Italy (Emilia Romagna region) and chamotte (ground fired ceramic scraps).

The raw materials described were included in different percentages within the mixture depending on their function: 45 wt% the plastic component, about 35 wt% the flux component, and about 20 wt% the inert component. The formulations taken as reference, L0 and P0 in Table 1, were developed in a previous work (Altimari et al., 2023).

Table 1

Batch prepared with pumice-based or lapillus-based bodies by replacing German ball clay with Italian kaolinitic clay. All values are in percentages (%).

	L0	L25	L50	L100	P0	P25	P50	P100
German ball clay	35	26	17.5	–	35	26	17.5	–
Italian kaolinitic clay	2	11	19.5	37	2	11	19.5	37
Italian kaolin	8	8	8	8	8	8	8	8
Lapillus	15	15	15	15	–	–	–	–
Pumice	–	–	–	–	16	16	16	16
Italian feldspar	19	19	19	19	17	17	17	17
Italian sand	3	3	3	3	5	5	5	5
Chamotte	18	18	18	18	17	17	17	17

Starting from these formulations, German ball clay was gradually replaced by Italian kaolinitic clay at 25%, 50% and 100% in order to evaluate the influence on technological properties as the percentage of replacement increased. The batches differed from each other in the presence of lapillus rock or pumice rock, so for simplicity below we will refer to lapillus-based or pumice-based products. The two clays have been characterized chemically, mineralogically, and thermally. The chemical and mineralogical characterization of the different raw materials was carried out and provided by the manufacturers of those raw materials. The thermal behavior of the clays was evaluated in terms of reactivity and weight variation with increasing temperature using differential thermal and thermogravimetric analysis. TGA/DTA analyses were performed with a NETZSCH STA 429 CD simultaneous thermal analyzer. The analysis was performed at a heating rate of 10 °C/min on ground samples with average particle diameters <20 µm.

The formulations prepared can be seen in Table 1. The letters L and P designate the lapillus-based or pumice-based mixtures respectively, the following numbers indicate the percentage of substitution of German ball clay in favor of Italian kaolinitic clay (e.g. L25 indicates a mix containing volcanic lapillus scraps with 25 wt% of Italian kaolinitic clay and 75 wt% of German ball clay, the percentages calculated refer to the clay component only).

Before further testing, all raw materials were dried in an oven at 150 °C ± 5 °C for 4–5 h. The slip was obtained by mixing in a fast ball mill (7 min) the raw materials with water in a ratio of 1:0.45 with a commercial deflocculant to increase the workability of the mixture; then the slip was dried, ground and moistened to 6%. Using a hydraulic press, the powders were compacted (pressure of 70–75 MPa) to obtain samples with a diameter of 50 mm for firing (industrial cycle: 48 min at 1210 °C) and with dimensions of 50 mm × 100 mm for calculating the flexural strength. These pressures are much higher than those normally used for laboratory samples, but they make it possible to compensate for the effect of the refractory support used for firing in an industrial kiln (the firing mode used for the samples under study).

2.2. Slip and green samples characterization

The slip is characterized by evaluating efflux time, density, and residual fraction.

The efflux time was calculated as the time required to empty a Ford cup with a nozzle diameter of 4 mm.

Density was calculated in accordance with Eq. 1 by placing the obtained suspension inside a pycnometer with a capacity of 1000 cm³ and of known weight:

$$d \text{ (kg/cm}^3\text{)} = (w_{p+s} - w_p) / 1000 \quad (1)$$

where: d is density, w_{p+s} is the total weight represented by pycnometer plus sample (kg) and w_p is the pycnometer weight (kg).

The residual fraction was calculated using a sieve with a mesh diameter of 63 µm by running slip through it and weighing the remaining solid mass on the sieve after drying.

The flexural strength was calculated on a minimum of four unfired ceramic samples (green) measuring 50 mm × 100 mm, using a Gabrielli Technology mini-CRC 2 Chrometer. The flexural strength on green was calculated because the tile must be able to withstand static and dynamic loads during the movement inside the factory. According to the standard, the tile is placed, like a beam, on two rollers at a distance from each other and a central force is applied by a third roller, which allows the breaking load to be determined, i.e., the weight that the specimen can support before it breaks. The breaking modulus (σ) is calculated from Eq. 2b, once the breaking stress (S) is known, which is equal to the product of the force applied to the working surface (F) and the ratio of the roller spacing to the tile width (L/b) as reported in Eq. 2a (Palmonari and Timellini, 2016).

$$S(N) = F \cdot L/b \quad (2a)$$

$$\sigma = 3FL/2bh^2 \quad (2b)$$

2.3. Fired samples characterization

2.3.1. Physical properties

Using Eq. 3, the weight loss (WL) was calculated:

$$WL(\%) = (w_i - w_f)/w_i \cdot 100 \quad (3)$$

where w_i is the weight of the green sample and w_f is the weight of the fired sample.

The dimensional variations of the samples after firing, at five different points, were measured using an electronic caliper (accuracy: ± 0.01) to obtain the linear shrinkage (LS) value, according to Eq. 4.

$$LS(\%) = (d_i - d_f)/d_i \cdot 100 \quad (4)$$

where d_i is the diameter of unfired pieces (50 mm) and d_f is the diameter of the sample after firing.

The water absorption under vacuum with automatic cycles of porcelain tiles was measured by placing the samples after firing inside a laboratory instrument (ISOVACUUM 650, Gabbrielli Technology) according to ISO 10545 standards. Water absorption (WA) is a parameter that determines the classification of ceramic tiles based on their open porosity. Porcelain stoneware belongs to the BIa group with WA (%) 0.5% (B means the product was formed by pressing).

2.3.2. Mineralogical analysis

Mineralogical analysis was performed on the clays and the fired samples in order to assess whether or not new crystalline phases were formed as a function of the amount of Italian kaolinitic clay substituted compared to those found in the samples containing German ball clay taken as reference. The patterns have been recorded on the powdered samples ($< 38 \mu\text{m}$ in size) for the clays and entire for the fired samples (specimen length 10.00 mm) in the $5-70^\circ 2\theta$ range (step size 0.013° and 1 s counting time for each step), operating at 40 mA and 40 kV mA at room temperature. The measures were conducted using an X-ray diffractometer from PANALYTICAL model Empyrean, with Ni-filtered $\text{Cu K}\alpha$ radiation using brackets holder. The identification of the crystalline phases occurred using the software Highscore Plus software version 3.0.

2.3.3. Microstructural analysis

Microstructural investigation was performed in order to evaluate the effect of the replacement of German ball clay with Italian red one. The instrument used is an environmental scanning electron microscope (ESEM-Quanta 200), combined with an X-ray EDS microanalysis system (X-EDS Oxford INCA-350). The fired samples analyzed were reduced to appropriate size ($< 1 \text{ cm}$ per side) and were metallized with a gold layer of a few nanometers to make the sample conductive.

2.3.4. Colorimetry

The change in the aesthetic properties of the samples and was evaluated by colorimetric testing with a UV-vis spectrophotometer (SPECTROPHOTOMETER CM-2600d, KONIKA MINOLTA), which operates in the $CIE L^*a^*b^*$ color space, allowing the set of colors perceived by the human eye to be described.

The analysis was performed by taking measurements at four different points on the sample surface to calculate the average values of $L^*a^*b^*$. Once these values are known for each sample, the parameter ΔE^* can be calculated by comparing two samples with each other, Eqn 5.

$$\Delta E^* = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} \quad (5)$$

Values of $\Delta E^* > 1$ indicate that there is visible difference between two samples.

3. Results and discussion

3.1. Characterization of clays

The clays were characterized chemically, mineralogically and thermally to assess the similarities and differences between them.

Chemical and mineralogical analysis can be seen in Table 2.

Chemical analysis, performed by X-ray fluorescence spectroscopy and provided by the raw material producers, allows to say that the two clays are comparable to each other in terms of SiO_2 and Al_2O_3 contents. The kaolinitic clay have a higher Fe_2O_3 content than the ball clay but a lower TiO_2 content therefore the sum of the chromophores seems to be comparable in the two cases. The presence of higher Fe_2O_3 content could change the densification process as observed by other authors (Jiang et al., 2017; Nawaukkaratharnant et al., 2022; Ismail et al., 2017). The Italian kaolinitic clay contain a high Na_2O content, and a slightly higher K_2O content. The alkali oxides increase the fusibility of the system (Bayer Ozturk and Ay, 2012) and thus could prolong the liquid phase and risk obtaining a less sintered product. The sum of alkali-earth oxides, CaO and MgO , is 0.86% for German ball clay and 1.46% for Italian kaolinitic clay. On the other hand, ball clay shows a higher loss by combustion than the kaolinitic clay, probably this could be due to the presence of organic carbon and sulfur.

The quantitative mineralogical analysis showed that the two clays are equal in quartz and kaolinite content. Ball clay contains more illite while kaolinitic clay contains illite and feldspar. Higher illite content results in more plasticity so Italian kaolinitic clay will be less plastic. The potassium in the German ball clay most likely can be linked to the presence of illite while the sodium, calcium and potassium detected in the Italian kaolinitic clay could be linked to the presence of plagioclase and orthoclase.

The thermal analysis performed on German ball clay is shown in Fig. 1 while on Italian kaolinitic clay in Fig. 2. The red curve (TG) shows

Table 2

Chemical, elemental and quantitative mineralogical analyses of clays (Font: Ceramic suppliers).

Chemical analysis		
Oxide (wt%)	German ball clay	Italian red clay
SiO_2	65.5	67.1
Al_2O_3	21.2	19.8
Fe_2O_3	1.86	2.5
TiO_2	1.27	0.8
CaO	0.32	0.72
MgO	0.54	0.74
K_2O	2.22	2.5
Na_2O	0.22	1.8
L.O.I.	6.66	5
Elemental analysis		
(%)	German ball clay	Italian red clay
C	0.17	0.18
S	0.1	0.05
Mineralogical analysis		
(%)	German ball clay	Italian red clay
Quartz	39	40
Kaolinite	33	34
Illite/Mica	23	14
Plagioclase/Orthoclase	–	8
Other	5	–

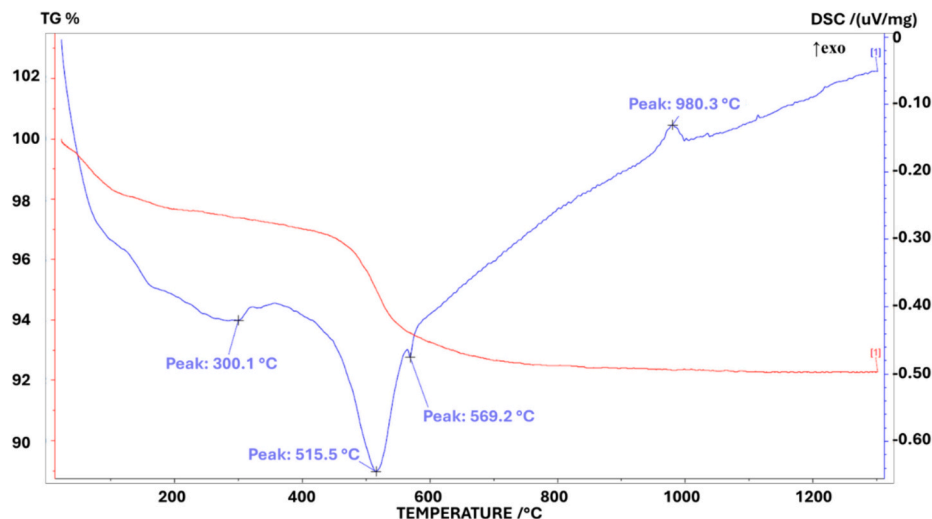


Fig. 1. Thermal analysis of German ball clay.

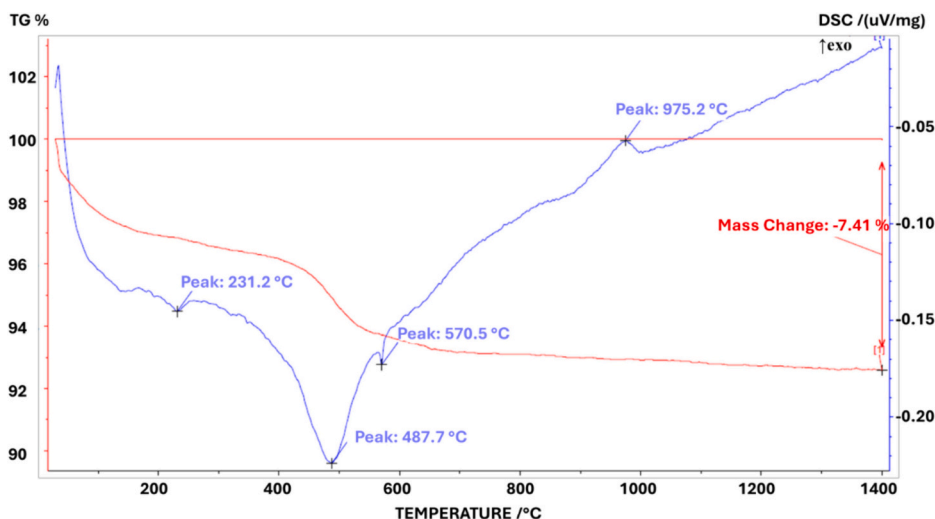


Fig. 2. Thermal analysis of Italian kaolinitic clay.

the weight loss while the blue curve (DTA) describes the *endo-exo* events:

- Total weight loss is slightly lower in the case of kaolinitic clay (~ 7.4% vs. ~ 8%) confirming the LOI results;
- The endo event loss of zeolitic water occurs up to higher temperatures for ball clay, but is quantified as a weight loss of about 3% in both cases;
- At temperatures between 487 °C and 570 °C, the endo events are associated to the dehydroxylation, most likely the second peak, which occurs at the same temperature in the two clays, is given by the transformation of kaolinite to metakaolinite with loss of the water of crystallization, resulting in a large weight loss;

- Around 980 °C for ball clay and around 975 °C for kaolinitic clay, there is an exothermic peak probably related to the formation of mullite without weight variation.

3.2. Slip and green samples characterization

Table 3 shows the variation of the analyzed parameters on the slip and unfired samples.

Considering the efflux time, it is possible to say that as the Italian kaolinitic clay content increases this parameter tends to increase. In the case of the lapillus-based mix it is possible to note that, except in the sample containing 100% Italian kaolinitic clay, the values obtained are still acceptable as an industrial parameter. Most likely, in the measurement of the efflux time of sample L100, a problem occurred, such as

Table 3

Analyzed parameters on slip and unfired samples.

	L0	L25	L50	L100	P0	P25	P50	P100
Efflux time (s)	16 ± 0.5	18 ± 0.5	22 ± 0.5	n.a.	21 ± 0.5	22 ± 0.5	37 ± 0.5	n.a.
Density (kg/m ³)	1.731 ± 0.050	1.727 ± 0.050	1.725 ± 0.050	1.773 ± 0.050	1.723 ± 0.050	1.714 ± 0.050	1.717 ± 0.050	1.732 ± 0.050
Residual fraction (g)	3.65 ± 0.01	3.91 ± 0.01	4.14 ± 0.01	4.88 ± 0.01	3.48 ± 0.01	3.59 ± 0.01	3.68 ± 0.01	4.14 ± 0.01
Green flexural strength (MPa)	40.28 ± 0.50	42.21 ± 0.50	39.64 ± 0.50	37.83 ± 0.50	41.3 ± 0.5	34.03 ± 0.50	28.07 ± 0.50	26.05 ± 0.50

a few grains clogging the outlet hole, and did not allow its proper evaluation. In the case of the pumice-based mixture, on the other hand, already with the substitution of 50% clay, the efflux time turns out to be high; therefore, as a result, the efflux time for sample P100 could not be evaluated. The limit value of efflux time, which can be considered acceptable at laboratory scale, is 50 s.

The value of density is related to the efflux time one, normally as efflux time increases, density also increases. As can be seen in both cases, the formulations containing 100% substitution, and which exhibited unmeasurable efflux time values showed higher density values. In general, density tends to maintain similar values up to 50% replacement rates in both the lapillus-based and pumice-based mixtures. To decrease density values and obtain measurable viscosity values, it will be necessary to add more water during grinding.

The residual fraction represents an important process parameter, and by looking at the values given in the table it is possible to say that this increases as the content of Italian kaolinitic clay inserted increases. In all cases the grinding time of the mixtures was 7 min. Most likely as the content of Italian kaolinitic clay within the mix increases, it will be necessary to extend the grinding time by a few minutes (at laboratory scale).

During the production process, the tiles must resist the stresses to which they may be subjected during transport within the plant to move from one production stage to another; for this reason, the flexural strength on the unfired product was calculated. In the case of the lapillus-based mix, the flexural strength tends to decrease as the percentage of clay replacement increases but still remains at fairly high values. In the case of the pumice-based mixture, however, the only acceptable value is the one obtained with 25% clay replacement since in the other two cases the values are very low (minimum acceptable value 35 MPa). The green bending strength is positively correlated with the kaolinite content and negatively related to the coarser particle fraction as reported by [Dondi et al. \(2023\)](#). It must be considered that these are still process parameters that can be improved by modifying the recipe and perhaps substituting some raw materials.

3.3. Characterization of fired samples

3.3.1. Physical properties

The physical properties analyzed were loss of ignition, water absorption and linear shrinkage whose values are reported in [Table 4](#).

Weight loss (WL) values are comparable with each other. The mixture containing a higher percentage of Italian kaolinitic clay has lower losses to the fire, this may be due to a lower presence of organic substances in Italian kaolinitic clay than the German ball clay.

The Italian kaolinitic clay has a coarser grain size than the German ball clay and, this can be inferred from the residual fraction values ([section 3.2](#)). The presence of harder minerals such as quartz and kaolinite led to a larger grain size, which may have changed the firing behavior of the samples. Italian kaolinitic clay is less plastic, and the increase in porosity could be due to this, as porosity may have been created on the green during pressing. Clays with higher illite content are more plastic and tend to fill the pores better during pressing. A less plastic clay with a larger grain size might have led to a different result than would be expected: usually, as the average grain size increases, water absorption increases and linear shrinkage decreases ([Jiang et al., 2017](#); [Fantini et al., 2024](#); [Nawaukaratharnant et al., 2022](#)). However, these unconventional porcelain stoneware bodies, as shown in previous

work by the authors, tend to have the opposite behavior: if shrinkage increases, absorption increases in turn ([Altamari et al., 2023](#)). A higher presence of quartz and kaolinite (2%) in Italian kaolinitic clay compared to German ball clays made the mixture more refractory. The presence of feldspars in kaolinitic clay contributes to sintering and thus to increase linear shrinkage during firing. Again, iron increases the liquid phase around temperatures of 1130 °C ([Jiang et al., 2017](#)) helping the densification phase and increasing linear shrinkage. However, the presence of iron also goes to affect water absorption values because, during firing, as it reduces, it contributes to gas formation by creating porosity and increasing absorption.

It should be kept in mind that compositionally there are not great differences between the two clays, however, in this case, the variables to be considered increase because of the starting mix, which is not a conventional porcelain stoneware mix since it contains rocks such as pumice or lapillus that affect the behavior of the starting material.

In general, it is possible to say that the water absorption values are very different between pumice-based and lapillus-based mixtures. In each case, as the Italian kaolinitic clay content increases, this value tends to increase, but all values are <0.5% (B1a group).

The linear shrinkage values are higher in samples L100 and P100 than in L0 and P0. It is possible to hypothesize that the higher presence of fluxing components (Fe_2O_3 , MgO , CaO , Na_2O , K_2O) in the Italian clay (8,26%) respect to German clay contribute to the sintering and densification process.

3.3.2. Mineralogical analysis

Mineralogical analysis was performed on all fired samples ([Figs. 3–4](#)). In [Figs. 3 and 4](#), the lower curves represent the spectrum of sample L0 and P0 respectively, that is, those with German ball clay, while the upper curves are for samples L100 and P100 respectively, thus containing only Italian kaolinitic clay. In both figures, a raised curve can be seen on the right side between the 5°–33° 2 Theta positions of the spectra, indicating the presence of a glassy phase, normally present in this type of body.

Porcelain stoneware is undergoing to complex transformations during firing with regard to the mineral components of the mixture. The resulting products contain a vitreous phase that can normally be associated with quartz, mullite, and feldspars. Quartz (SiO_2) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) were detected in both batches of products. Clay minerals around 1000 °C form mullite due to the reaction between Al_2O_3 and SiO_2 , contained in the raw materials, especially kaolinitic ones ([Nawaukaratharnant et al., 2022](#)). The formation of mullite is very important for the mechanical properties of porcelain stoneware.

The lapillus-based batch also showed the presence of feldspars, orthoclase ($\text{K Al Si}_3 \text{O}_8$) and albite ($\text{Na Al Si}_3 \text{O}_8$). As the content of Italian kaolinitic clay increases, the content of SiO_2 and K increase in the mixture, and the intensity of quartz peaks tends to increase as well as that of orthoclase.

In the pumice-based batch, unlike the lapillus-based batches, both mullite and quartz peaks tend to decrease this despite the fact that the amount of iron in the mixture is lower ([Nawaukaratharnant et al., 2022](#)); this could be due to a higher presence of potassium contributed not only by Italian kaolinitic clay but also by pumice ([Barbieri et al., 2023](#)).

3.3.3. Microstructural analysis

ESEM images of the lapillus-based samples can be observed in [Fig. 5](#)

Table 4
Weight loss (WL %), water absorption (WA %) and linear shrinkage (LS %) of fired samples.

	L	L25	L50	L100	P	P25	P50	P100
WL (%)	3.29 ± 0.10	3.35 ± 0.10	3.24 ± 0.10	2.94 ± 0.10	3.70 ± 0.10	3.50 ± 0.10	3.11 ± 0.10	3.31 ± 0.10
WA (%)	0.05 ± 0.01	0.10 ± 0.01	0.06 ± 0.01	0.19 ± 0.01	0.12 ± 0.01	0.22 ± 0.01	0.35 ± 0.01	0.47 ± 0.01
LS (%)	4.46 ± 0.05	4.46 ± 0.05	4.94 ± 0.05	6.12 ± 0.05	4.94 ± 0.05	5.36 ± 0.05	5.56 ± 0.05	5.66 ± 0.05

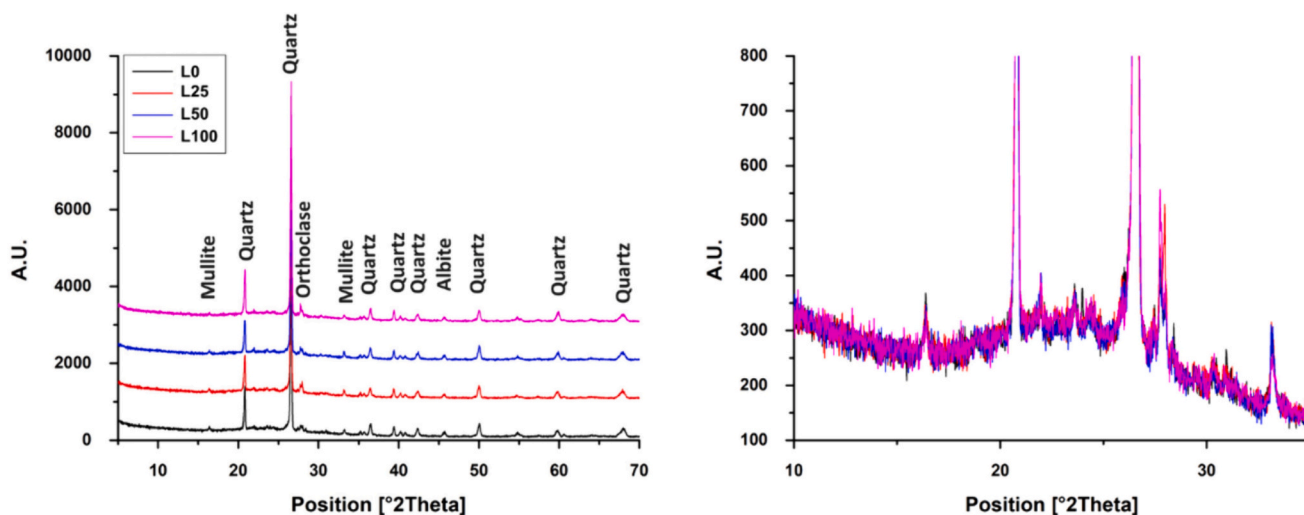


Fig. 3. Mineralogical analysis on lapillus-based materials. On the left are spectra of the formulations, with the percentage of Italian kaolinitic clay increasing from bottom (L0) to top (L100). On the right, magnification between 10 and 30 2 theta to highlight the presence amorphous phase.

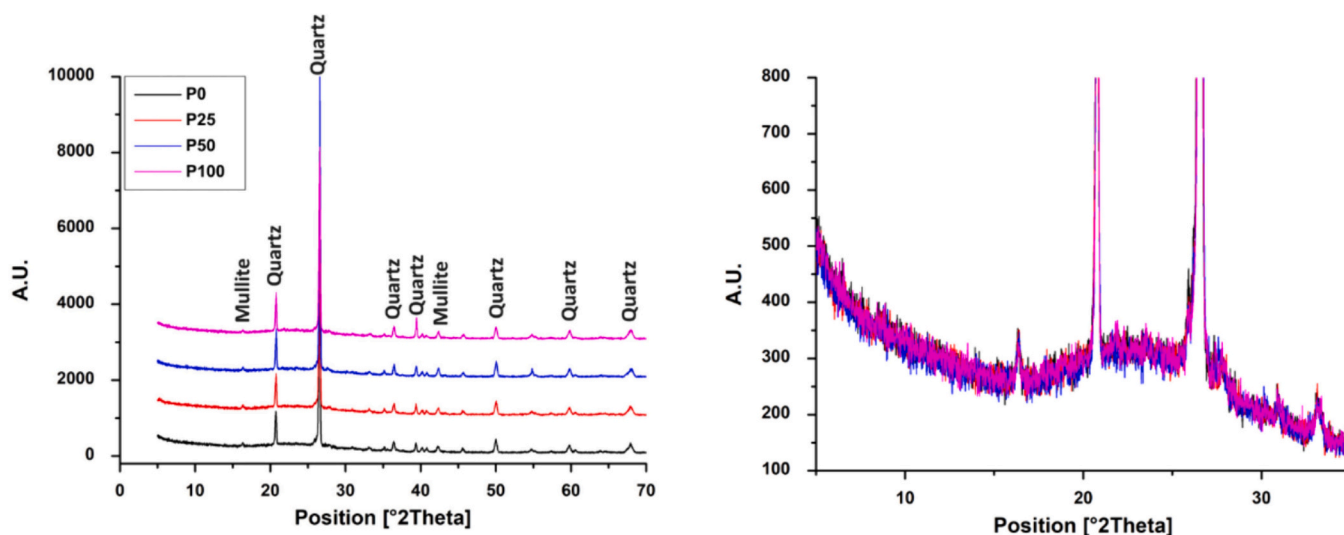


Fig. 4. Mineralogical analysis on pumice-based materials. On the left are spectra of the formulations, with the percentage of Italian kaolinitic clay increasing from bottom (P0) to top (P100). On the right, magnification between 10 and 30 2 theta to highlight the presence amorphous phase.

(a-d). The images were acquired in secondary electron mode. Images (a) referring to sample L0 show diffuse porosity, with pores of various sizes. There are many small pores ($<10\ \mu\text{m}$) and some larger ones that reach sizes on the order of $45\text{--}50\ \mu\text{m}$. Looking at the L25 (b), L50 (c) and L100 (d) samples, it is possible to see that as the Italian kaolinitic clay content increases, the porosities continue to be widespread but the small pores decrease and the larger ones increase. It would also appear that the shape of the porosities is more regular in the sample containing only German ball clay and that as the percentage of clay replacement increases pores show increasingly irregular shapes. The presence of the diffuse porosity and the increase in pore size also confirm the results obtained from the water absorption; this adsorption increases, making the material less resistant to stress due to the voids that are formed.

A further observation that can be made is related to the presence of the amorphous phase, which seems to increase as the amount of German ball clay decreases, and these results appear to agree with the diffractometric analysis performed on the samples, where the presence of glassy phase was revealed.

Sample L0 compared to the other samples appears to be more sintered while L100 is the one that would appear to be less densified.

ESEM images of the pumice-based samples can be observed in Fig. 5 (a-d). The P0 sample, identified by (e), shows a spherical porosity with a size of $10\ \mu\text{m}$ and an intergranular porosity with a size of $30\ \mu\text{m}$; the pores are larger in size than in the lapillus-based sample containing only German ball clay. Also in the pumice-based samples, as happened in the lapillus-based samples, as the Italian kaolinitic clay content increases, the porosity increases in both size and quantity. Samples P25 (f), P50 (g) and P100 (h) have much larger pores than their lapillus-based analogs, and this could strongly affect the flexural strength values on the fired pieces.

The pumice-based samples appear less sintered than their P0 reference, but they also appear less sintered than the lapillus-containing samples. The amorphous phase present could also be attributable to a lower degree of sintering or to an overfiring of the samples at the industrial temperatures due to the high amount of amorphous fraction.

3.3.4. Colorimetry

The $CIE\ L^*a^*b^*$ system, which is widely used in the ceramic industry, has made it possible to obtain colorimetric data. The parameters determined and processed by the visible spectra were the lightness (L^*),

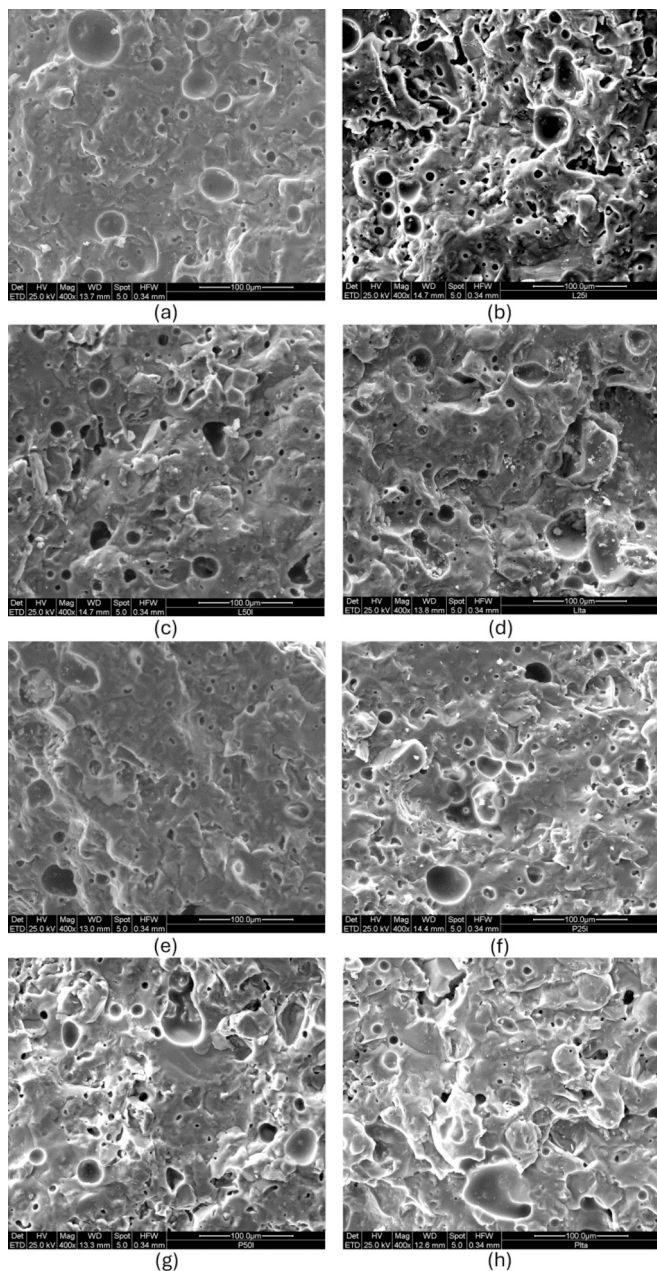


Fig. 5. ESEM images of lapillus-based and pumice-based samples. (a) L0, (b) L25, (c) L50, (d) L100, (e) P0, (f) P25, (g) P50, (h) P100.

which can vary between 0, corresponding to absolute black, and 100, corresponding to absolute white, a^* , which describes the variation of the reds and greens, and b^* , which describes the variation of the yellows to blue. The values obtained are shown Table 5.

The reported values of ΔE^* were obtained from the comparison with the L0 and P0 samples depending on the mixtures considered.

Looking at the values obtained for both the lapillus and the pumice samples, it can be seen that the brightness decreases with the increase of Italian kaolinitic clay in the mixture, while a^* and b^* , on the contrary, increase. Only in the case of P100, ΔE^* is lower than in the case of P50. In the case of the pumice-based mixtures, the initial value of L^* is higher due to a minor amount of iron in the composition. Regarding the ΔE^* value is also strongly influenced by the fact that the brightness tends to decrease with greater variation from one sample to another. The variation in the values shown in the table can be related to a major presence of Fe in the Italian kaolinitic clay. The colorimetric difference

Table 5

CIELab* values obtained for the best samples compared to the reference.

	L^*	a^*	b^*	ΔE^*
L0	46.54 ± 0.60	1.76 ± 0.03	5.45 ± 0.07	–
L25	43.90 ± 0.20	1.83 ± 0.07	5.51 ± 0.10	2.65 ± 0.40
L50	43.27 ± 0.20	2.10 ± 0.03	5.53 ± 0.04	3.29 ± 0.40
L100	38.87 ± 0.35	3.33 ± 0.03	5.50 ± 0.07	7.83 ± 0.25
P0	51.07 ± 0.40	3.55 ± 0.05	9.74 ± 0.15	–
P25	49.58 ± 0.36	4.26 ± 0.05	9.53 ± 0.09	1.66 ± 0.04
P50	46.22 ± 0.80	5.83 ± 0.10	10.20 ± 0.14	5.38 ± 0.34
P100	42.51 ± 0.33	6.10 ± 0.15	8.99 ± 0.25	8.96 ± 0.09

obtained highlights the achievement of a darker support than the previous one. This difference is positive in this case as the support tends to take on a color very close to some brown glazes currently produced in the ceramic company.

4. Conclusions

Ceramic supports were formulated containing German ball clay, which was progressively replaced by Italian kaolinitic clay, all with the aim of obtaining a body consisting in Italian raw materials. The reference mixes, one based on L0 volcanic lapillus scraps, and one based on P0 pumice, were naturally colored porcelain stoneware slurries, therefore Italian kaolinitic clay was replaced German ball clay to evaluate the technological and aesthetic properties.

The lapillus-based mixtures studied showed low absorption, rather high linear shrinkage, particularly sample L100, and an internal microstructure similar to that of porcelain stoneware. In this case, the German ball clay could theoretically be totally replaced, resulting in a porcelain stoneware mix containing only Italian raw materials.

Pumice-based mixtures have shown, with replacement percentages of Italian kaolinitic clay exceeding 50%, a water absorption at the limit of what is required by the standard for a product to be classified as porcelain stoneware. In this case, it is possible to partially substitute the German ball clay, up to 25%, to obtain technological properties similar to commercial porcelain stoneware.

In both batches, the internal microstructure of the samples changed. Although the obtained samples, by water absorption values, could be considered as belonging to the BIa group, ESEM analysis showed that there was an increase in closed porosity and that some particles had not fully reacted. The densification process took place, as evidenced by an increase in the linear shrinkage value. However, the water absorption value did not drop to zero. Italian kaolinitic clay is less plastic and the increase in porosity could be due to this; therefore, although a total substitution in the lapillus mix is possible, it would be better not to completely replace the German ball clay in order to control the formation of pores and improve the technological properties of the finished products.

CRedit authorship contribution statement

Fabiana Altamari: Writing – review & editing, Writing – original draft, Investigation, Data curation. **Fernanda Andreola:** Writing – review & editing, Formal analysis, Data curation. **Isabella Lancellotti:** Writing – review & editing, Validation, Conceptualization. **Luisa Barbieri:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Comparative life cycle analysis between commercial porcelain stoneware and new ones designed by using volcanic scraps

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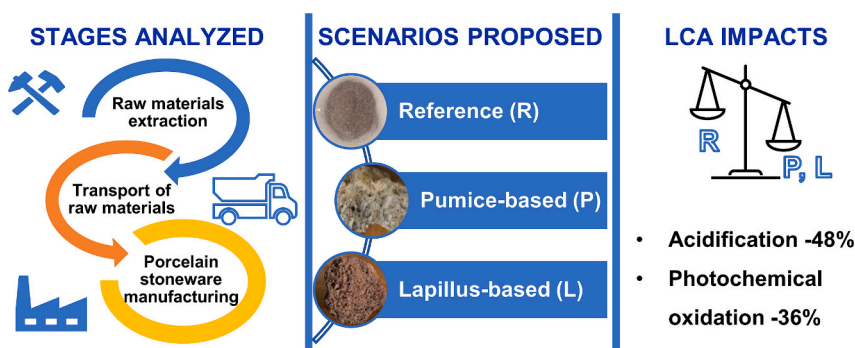
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HIGHLIGHTS

- Comparative LCA was performed on three porcelain tiles, two of them with scraps
- Environmental benefits of pumice and lapillus-based products have been evaluated
- Products with scrap had a lower environmental impact than the reference product
- The pumice-based product showed lesser impacts than the same with lapillus
- "Acidification" category showed approximately 48 % reduction in impact

GRAPHICAL ABSTRACT



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ABSTRACT

To achieve carbon neutrality by 2050, many companies have started implementing sustainability policies. The aim of this work, as result of collaboration between Universities and companies, is to assess the environmental impacts associated with the production of alternative formulations of porcelain stoneware. The proposed formulations contain extraction scraps and chamotte and have promising technological properties. A comparative analysis of the life cycle in three different scenarios was carried out to assess the environmental footprint of the final products. The analyzed scenarios were a glazed porcelain stoneware (which was taken as a reference and is commercially available), a porcelain stoneware containing pumice scraps, and one containing volcanic lapillus scraps. It was observed that the transportation of raw materials has the largest environmental impact, followed by the production and extraction of the raw materials themselves. From the performed analysis, it was possible to observe that by replacing the currently used materials by the ones hereby studied, environmental benefits can be obtained. In particular, depending on the considered pollutant, the environmental impact can be reduced between a minimum of about 8 % (Freshwater Aquatic Ecotoxicity category) to a maximum of 48 % (Acidification category). In a time when raw materials supply is difficult, the use of scraps, which would otherwise be disposed of, is particularly interesting and can lead to the production of an environmentally friendly product.

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1. Introduction

The manufacturing of building materials is one of the most environmentally impactful processes globally. The decarbonization of this sector must be achieved by 2050. However, there has been an upward trend in energy consumption and emissions since 2020, due to production increases. The construction sector accounts for about 40 % of European energy demand but 80 % of the energy comes from fossil fuels. In 2021, this sector was responsible for CO₂ emissions for about 37 % globally and consumed about 34 % of the global energy demand (Anon, 2023a).

The impact of construction on the environment is not only limited to energy consumption and carbon dioxide emissions but there are also consequences on the ecosystem such as, for example, consumption of land and resources, such as water and raw materials. Further, the effects on the environment caused by the extraction, processing and transportation of these materials are to be considered. Sometimes, the effect of transportation is so important that it can make not sustainable even products that are green from a technological point of view.

Ceramic tiles belong to building materials: Italy is the seventh largest producer worldwide and second largest in Europe (Baraldi, 2023). The Italian production chain is designed with sustainability as a priority. Indeed, 100 % of raw, fired waste, and wastewater are fed back into the production cycle. Moreover, 47 % of energy is self-produced, and 99 % of dust is filtered (Anon, 2023b). Although ceramic tile production has lower CO₂ emissions than clinker production, the supply chain of raw materials must be considered: the raw materials for clinker production are located near the production plants while more than 50 % of the raw materials for ceramic tile production comes from abroad by sea, rail, or road (Anon, 2023c). Over the years, numerous studies have been carried out on the incorporation of waste into ceramic tiles. The main results regarding the effect of waste on the technological behavior and environmental impact resulting from the production of these products have been evaluated by Zanelli et al. (2021).

The demand for environmentally sustainable buildings is constantly increasing. Nonetheless, it is necessary to make products that can be not only environmentally friendly but with satisfying technological properties. Life cycle analysis (LCA) is a useful tool for understanding and minimizing the environmental impacts of products and services. As the world moves towards sustainability, LCA plays a crucial role in assessing and improving environmental performance by enabling the assessment of environmental impacts associated with all life stages of a product, process or service. The Society of Environmental Toxicology and Chemistry, in 1993 defined LCA as an objective process of assessing the environmental impacts associated with a product, process or activity by identifying and quantifying material and energy consumption and emissions to the environment and identifying and evaluating opportunities to reduce those impacts. Defining the boundaries of the system is very important as it allows to determine which processes, operations and flows should be taken into account: there may be several possibilities, for example, cradle to gate, cradle to grave and cradle to cradle. Referring to a product, the cradle-to-grave analysis covers the entire life cycle: from the extraction and processing of raw materials to the production, transportation, and distribution of the product, its use, reuse, and maintenance, to the recycling and final disposal of the product after use. In contrast, in the cradle-to-gate pathway the end of the scope is the factory gate (usually before the product is distributed to customers). It analyzes only up to the point where the product leaves the manufacturing facilities. The latter approach is sometimes preferred when the product can be easily recycled or composted, avoiding landfill, or simply because it is easier to track. ISO 14040 and 14,044 provide the framework for conducting LCA studies and define four main steps: 1. goal setting (ISO 14040); 2. inventory analysis (ISO 14041); 3. impact assessment (ISO 14042); 4. interpretation of results (ISO 14043). Each stage plays a key role in the analysis, enabling a detailed understanding of environmental impacts during the life of a product or service. Its

application can help identify critical areas for environmental improvement, assess the environmental performance of products and services, and support decision making in the selection of alternative materials or processes, the latter coinciding with the objective of this paper. Numerous LCAs have been performed on ceramic tiles to assess their ecological footprint. Waterkemper Vieira et al. (2023) analyzed different works concerning the Brazilian ceramic tile industry identifying the relationships between the variables affecting the forming process and highlighting the areas that need measures to reduce the environmental impact of production. This study found that the transportation of raw materials from quarries to factories is the stage that causes the greatest environmental impact while the glazing of tiles is the main contributor to environmental effects in the studied industries. Almeida et al. (2016) evaluated the environmental profile of ceramic tiles produced in Portugal through LCA from cradle to grave; the most impactful processes are due to site activities, transportation, power generation and natural gas production. Tikul (2014) analyzed the impacts caused by the production processes used by small and medium-sized ceramic tile companies in Thailand, observing that small companies are more energy-intensive and more impactful than medium-sized ones. Ma et al. (2022) conducted an environmental footprint assessment on China's ceramic tile manufacturing sector through an LCA study and a view of the energy-carbon-water nexus; the greatest impact in this case was direct emissions, energy, transportation, and solid waste. Morfino et al. (2022) analyzed through LCA the impacts from the use of bleaching materials incorporated within ceramic tile mixtures to provide manufacturers with a tool to guide their choices in the selection of matting materials. Andreola et al. (2007) and Barberio et al. (2010) evaluated the environmental impacts of using end-of-life cathode ray tube glass and municipal solid waste incinerator bottom ash for ceramic glaze production and demonstrated the benefits. Assumpção de Castro et al. (2023) evaluated the life cycle and environmental contamination of cement tiles while Atılgan Türkmen et al. (2021) analyzed different scenarios for tile production to understand which process was more sustainable. Other studies can be found in the literature that use LCA to compare the production of ceramic tiles with marble (Nicoletti et al., 2002) or to assess the environmental footprint of ceramic floor and wall materials and bricks (Bovea et al., 2007; Ibáñez-Forés et al., 2011; Fullana and Palmer, 2011; Quinteiro et al., 2014; López-García et al., 2021). Moreover, LCA is becoming an increasingly popular tool in the construction industry. In fact, it is possible to find LCAs carried out on different types of mortars, cements and concretes (Farinha et al., 2019; Cuenca-Moyano et al., 2017; Tosti et al., 2020; Kul et al., 2023; Manjunatha et al., 2021; Wang et al., 2023; Colangelo et al., 2018; Ouellet-Plamondon and Habert, 2015) and even on aggregates (Pradhan et al., 2019; Tefa et al., 2022; Uzzal Hossain et al., 2016; de Bortoli, 2023).

It must be considered that this methodology has limitations because there is always a tendency to make simplifications of the system when the model is built. This is needed to enable the evaluation of the model itself, but could lead to analyses that are not always comparable. If, for example two different boundaries are considered in the same analysis, a comparison cannot be made. In addition, it is also necessary to consider the type of data such as primary (provided by company), secondary (provided by databases or literature) or tertiary (estimated data). In particular, the latter two increase the uncertainty of the final results. Some studies in literature (Cellura et al., 2011; Santos et al., 2022) deal exactly with this issue. Further, the country or the time period (or both) can influence the results, therefore they cannot be applicable in a different context. The methods used to analyze impacts are also many, and the analyses obtained by using different methods lead to results that are not comparable to each other.

The goal of this paper is to evaluate comparatively the environmental impact of three porcelain stoneware tiles by the same LCA approach and software, and using the same borders, i.e., from the cradle to the gate. Commercial porcelain stoneware was the reference for two

new products formulated by replacing, in weight, foreign feldspars with approximately 50 % waste and scraps, of which 15–16 % are volcanic raw material scraps (pumice and lapillus). The technological performances of these products have already been analyzed by the authors in a previous paper (Altimari et al., 2023) and this research aims at completing the study by an environmental impact evaluation. The three types of porcelain stoneware have some raw materials in common: a German clay and some Italian raw materials. The mixture used as a reference was composed of 18 raw materials, while the mixtures based on pumice or lapillus scraps were made of 8 raw materials. In addition to the presence of pumice or lapillus, the two scraps-based bodies differ in the different percentages of used raw materials.

The novelty of this study is the application of the LCA approach to ceramic products obtained by exploiting Italian volcanic scraps, in order to help producers or customers to analyze advantages or drawbacks of these new raw materials.

2. Methodology

2.1. LCA methodology

The comparative environmental assessment described in this paper was performed according to the international regulatory reference for the execution of LCA studies represented by the ISO 14040 series of standards. The structure of LCA is divided into four main steps: objective and scope, life cycle inventory, impact assessment and interpretation of results (<https://www.csqa.it/it-it/certificazioni/sostenibilita/lca-iso-14040-14044>, n.d.).

2.2. Goal of the study

The focus of this work was to compare the environmental impacts of a commercial porcelain stoneware with two similar products containing mining and processing scraps of Italian volcanic minerals. The considered products have been engineered within a research and development cooperation between the academic and business worlds. The products have been technologically compared by the authors in Altimari et al.

(2023). With the results that will be exposed in this work, the authors wanted to complete analysis by evaluating the environmental impact of the product with a view to promoting commercial and productive transferability, in the context of the circular economy and national productive self-sufficiency.

Porcelain stoneware is usually composed of clays, feldspars and inert materials.

The products under study were a reference porcelain stoneware produced by a ceramic company that is part of the Sassuolo (MO) ceramic district (Italy), a porcelain stoneware containing pumice scraps and one containing lapillus scraps.

The raw materials used for the production of the reference sample were: two German clays, an Italian clay, an Italian kaolin, a mixture of five Italian feldspars and six Turkish feldspars, two types of Italian sands, and some raw and fired scraps from the production cycle.

The raw materials used for the production of samples containing pumice or lapillus were German clay, Italian clay, Italian kaolin, pumice or lapillus scraps (aluminosilicate raw materials that can be used as valuable raw materials in various fields (Barbieri et al., 2023)), scraps of an Italian feldspar, Italian sand, and two types of fired scraps from the production cycle. The mixture of foreign and Italian feldspars used for the reference support was replaced with pumice or lapillus scraps and Italian feldspar scraps.

The number of raw materials required to manufacture the product was reduced from 18 to 8. This led to a reduction in dye pigments while achieving good technological properties, as demonstrated in Altimari et al. (2023).

2.3. Functional unit and system boundaries

The studied system corresponds to stoneware tile. Therefore, its function is to provide coverage to the floor of a building. The chosen functional unit is 1 m² of tiles.

The LCA was carried out following a cradle-to-gate approach. The life cycle analysis was evaluated by several stages:

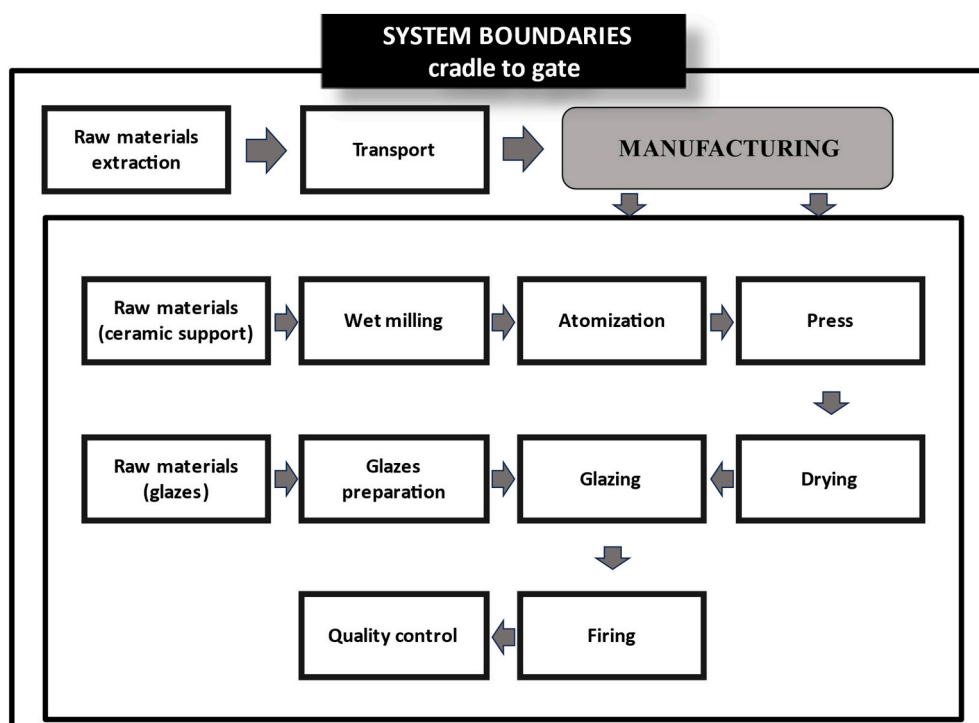


Fig. 1. System boundaries.

- Raw materials: in this phase, all materials needed to obtain support, engobe and glaze were considered. Processing scraps used as raw materials were considered to have neutral impact since they are not extracted specifically for the purpose. German and Italian clays, Italian kaolin, Italian and Turkish feldspars, pumice scraps, lapillus scraps and Italian feldspar scraps, Italian sands, scraps from the production cycle and dyes of various kinds were used to obtain ceramic support. Clays from Britain and Germany, German bentonites, German sands, Italian feldspars, northern European feldspatoids and ceramic frits from Spain were used to make engobes and glazes. In 2022, 347.5 tons of raw materials will be consumed in the plant for the production of the reference support only;
- Transportation: transportation of all raw materials from the respective quarries/mines to the production plant was considered in this phase. The routes were traveled by road, train, and sea. The distance traveled by road, to get from the quarries to the production plant, can be very different; there are local raw materials that travel about 12 km but there are also raw materials that come from abroad traveling about 1200 km. The same for transportation by sea, as Italian raw materials travel about 280 km while foreign raw materials can travel up to about 8050 km. Only one raw material, German clay, travels by train, so the distance is constant corresponding to 900 km;
- Production: this phase accounts for all the processes required to obtain the products with the related energy consumption and emissions generated to complete the process. The energy consumption considered in this phase also includes the packaging phase. The production is related to the manufacture of approximately 6.255.444 m² of porcelain stoneware produced in 2022 (considering that 18 kg of raw materials related to the substrate only are used for 1 m²). In all studied cases, the considered firing cycle is the one currently used by the company, i.e. a time of 48 min at a temperature of 1210 °C.

The scenarios considered in this investigation were:

- Reference porcelain stoneware scenario (REFERENCE), which describes the sourcing and transportation of raw materials to the factory and the production of the considered product
- Scenario of porcelain stoneware containing 16 % of pumice scraps (PUMICE-BASED), which in addition to accounting for sourcing, transportation, and manufacturing of the product, goes on to consider the non-extraction of some raw materials and the decrease in the use of coloring oxides (approx. 50 %);
- Scenario of porcelain stoneware containing 15 % of volcanic lapillus scraps (LAPILLUS-BASED), which contains less sand and more feldspars than the previous one (Altimari et al., 2023).

Fig. 1 summarizes the considered life cycle stages; these are the same for all three scenarios.

2.4. Assumptions and considerations

The following assumptions were made for each scenario:

1. The amount of mix to obtain 1 m² of tile is 18 kg (Assopiastrelle, 1997);
2. The selected means of transportation were those with lower emission levels (Euro 6 certified trucks, electric-powered trains);
3. The coloring oxides used to color the substrate are reduced by 50 % in the case of pumice-based and lapillus-based mixture, as they naturally color the ceramic piece (brown for pumice-based, black for lapillus-based);
4. All raw and fired waste is fed back into the production cycle.

Since there is no direct or good quality data, nor high interest because they are the same in all scenarios, the following parameters

were not considered within the process:

1. Emissions related to dust and fume removal systems (Soliroc™ process (Commissione delle Comunità Europee, 1997));
2. Waste production and disposal (for example insulators);
3. Water consumption, as this is recycled within the production cycle (<https://www.ceramica.info/articoli/ceramica-italiana-scelta-sostenibile-video-brochure/>, n.d.);
4. The energy produced in cogeneration;
5. Fuels used for vehicles loading hoppers.

2.5. Life cycle inventory analysis

Life cycle inventory analysis is a phase that includes the collecting and processing of data on all inputs and outputs of the production system under consideration. In order to obtain a valid model, the inventory must be as complete as possible.

Data on raw material extraction and transportation (not km traveled but related to fuels, emissions, ...) come from the Ecoinvent v3 database (Weidema et al., 2013; Frischknecht and Rebitzer, 2005). In this regard, the data on the processes that most closely resemble the objective and scope of this study were selected, with a global scope and sintering temperatures similar to those used in this life cycle study; data on transportation (km traveled), quantities of raw materials used, and energy consumption were primary data, i.e., provided directly by the tile maker company involved in this study.

Data on the quantities (kg) of raw materials needed for the annual production of porcelain stoneware were provided by the manufacturing company. Carriers deliver the raw materials needed for production every week; upon entering the company these are mandatory to declare the quantities delivered, which are then certified by the operators. The quantities are recorded and make it possible to obtain very reliable estimates of the raw materials purchased and used. The unit of measurement related to the quantities of raw materials was “kg”.

Raw material transport data, on the other hand, were provided by the mining companies. Distances were estimated on the basis of actual kilometers traveled by transporters (in the case of road routes), trains or ships. However, the data were checked and confirmed through the use of high-accuracy maps. The unit of measurement related to transportation was “tkm” (ton per km).

Regarding energy data, it must be considered that ceramic companies, being highly energy-intensive companies, are subject to mandatory energy diagnosis in accordance with Legislative Decree 102/2014. Energy diagnosis is defined as a procedure aimed at providing adequate knowledge of the energy consumption profile of industrial plant. Thus, the diagnosis is the most qualified tool for analyzing the energy management framework of an activity: it highlights the level of management efficiency, starting from the analysis of significant energy flows, to identify the most energy-intensive process steps and machines.

Electrical and thermal equipment consumption data were collected or calculated by:

- Field measurements of consumption (continuous meters, periodic readings of parameters for industrial management/accounting, ...);
- Spot readings of consumption by instrumentation inserted for periods deemed significant to the interpretation of the consumption trend of the equipment under consideration;
- Estimation of consumption based on nameplate powers, time of use of the equipment and the sensitivity of the department head in defining possible correction factors (average power consumed versus nameplate power).

In this case, for electricity consumption, the company has tax counters for purchase and production (co-generator); a tax counter also measures the consumption of natural gas taken from the pipeline.

The company in 2023 carried out the energy diagnosis, and the

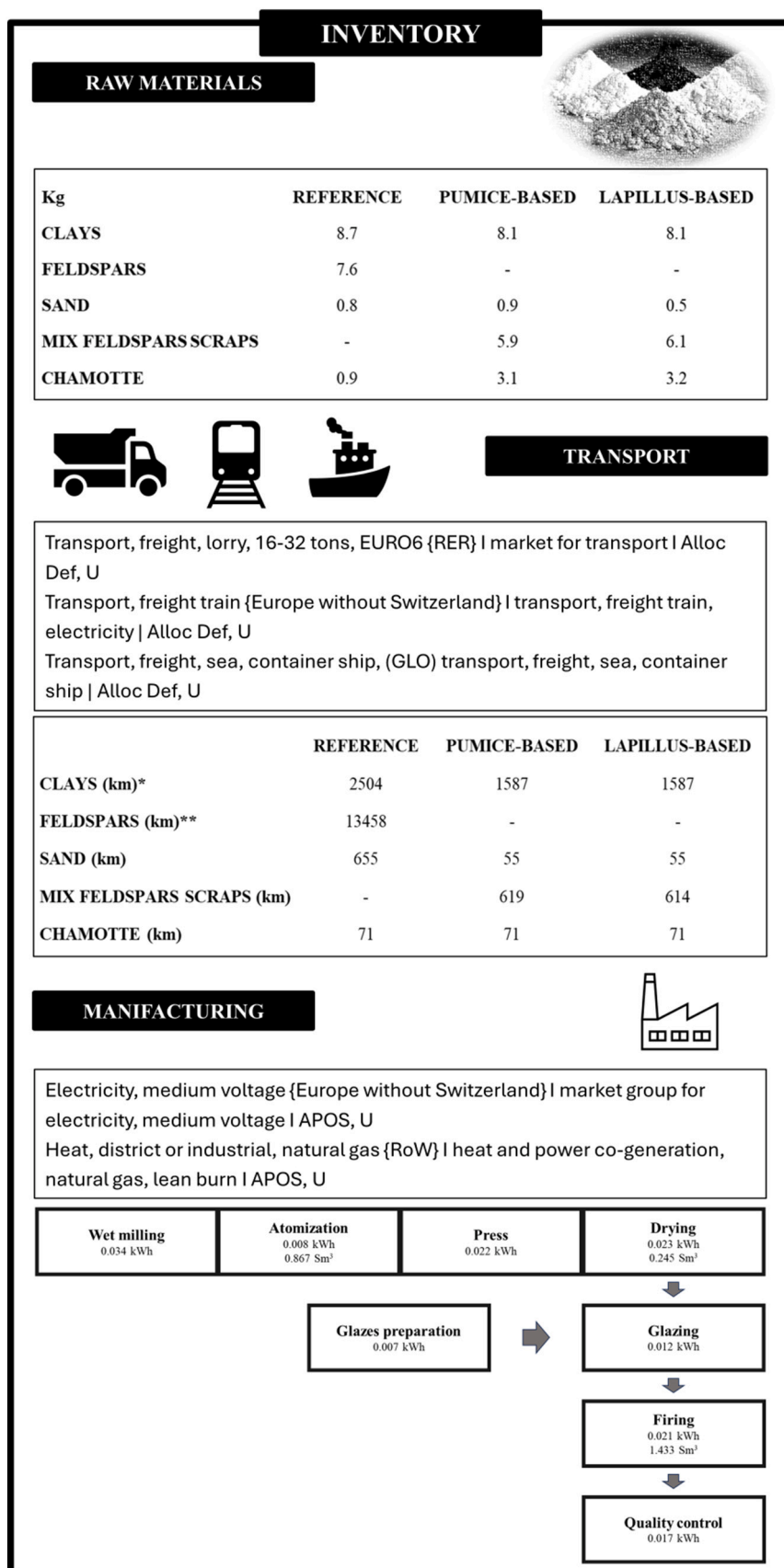


Fig. 2. Inventory data.

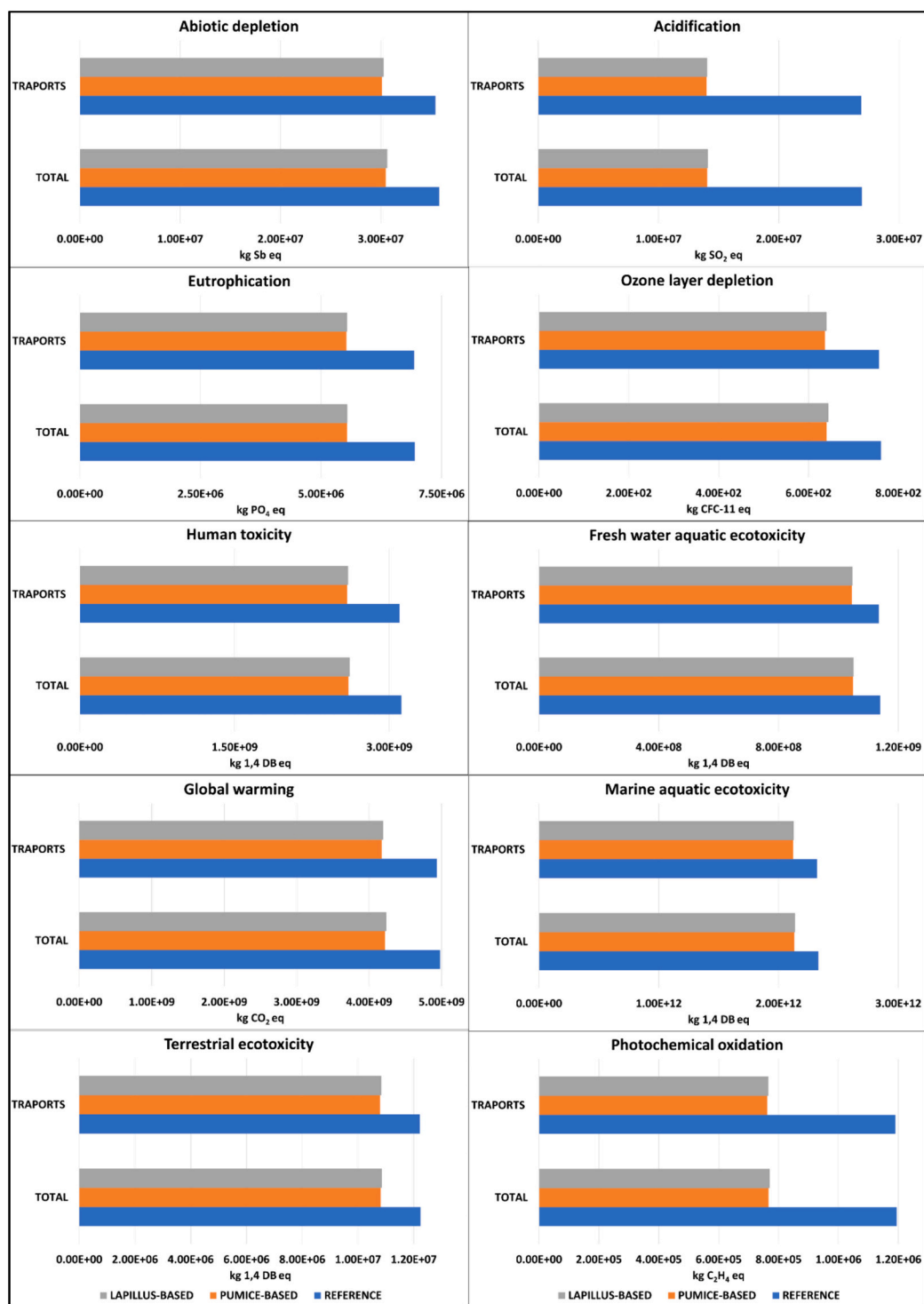


Fig. 3. Impact categories for the three scenarios.

expert staff who dealt with it validated the data reported in this paper. However, all data were rechecked to be sure of the quality of the input data and consequently have reliable output data. The unit of measurement related to energy was “kWh” and “Sm³” (Standard cubic meter).

Fig. 2 shows some inventory data for raw material, transportation and energy. It shows the quantities of raw materials needed to produce 1 m² of product and the distances traveled from the quarries to the factory. In terms of distances, the raw materials marked with an asterisk (*) are transported by road and rail, those marked with two asterisks (**) are transported by road, by rail and by sea, and all others are transported by

road. “Mix feldspars scraps” means the sum of pumice or lapillus scraps and Italian feldspar scraps.

Regarding the data on the consumption of electricity (kWh) and natural gas (Sm³) needed to produce 1 m² of product (data provided by the ceramic company), they are again visible in Fig. 2. Consumption was considered to be the same for every type of porcelain stoneware. The figure does not show consumption data for auxiliary and general services, which are 0.99 kWh and 0.06 Sm³ and 0.06 kWh and 0.004 Sm³, respectively.

For simplicity of visualization, the merged data have been shown in

Table 1

Impact percentages corresponding to raw materials (RM), transportation (T), and manufacturing (M).

	Reference (%)			Pumice-based (%)			Lapillus-based (%)		
	RM	T	M	RM	T	M	RM	T	M
Abiotic depletion	0.07	98.93	1.00	0.05	98.78	1.17	0.05	98.78	1.17
Acidification	0.08	99.76	0.16	0.09	99.60	0.31	0.09	99.60	0.31
Eutrophication	0.10	99.80	0.09	0.09	99.79	0.12	0.09	99.79	0.12
Global warming	0.07	99.06	0.87	0.05	98.93	1.02	0.05	98.93	1.02
Ozone layer depletion	0.08	99.46	0.46	0.07	99.38	0.54	0.07	99.39	0.54
Human toxicity	0.17	99.52	0.31	0.17	99.46	0.37	0.17	99.46	0.37
Fresh water aquatic ecotoxicity	0.18	99.66	0.16	0.18	99.65	0.18	0.18	99.65	0.18
Marine aquatic ecotoxicity	0.21	99.56	0.24	0.20	99.54	0.26	0.20	99.54	0.26
Terrestrial ecotoxicity	0.11	99.80	0.09	0.10	99.80	0.10	0.10	99.80	0.10
Photochemical oxidation	0.07	99.61	0.32	0.07	99.43	0.50	0.07	99.43	0.50

Fig. 2. As mentioned in Section 2.2, in the case of both quantities and transports, when it comes to clays, it must be considered that we are dealing with 4 types of them in the case of the reference and 3 in the other two cases while, in the case of feldspars, 11 were considered for the reference and 2 (mix feldspars scraps) in the other two scenarios. The sands included in the slurries were 2 in the reference scenario and 1 in the other two cases while for chamotte 1 type was used in the reference and 2 types for the pumice based or lapillus based scenarios.

Energy data have also been merged; the data visible in the Figure below refer to the sum of the data from the departments considered. For example, the grinding department refers not only to the operation of grinding raw materials, but to all the machinery that contributes to this stage: conveyor belts, automatic loading and unloading of raw materials, monitoring booths; the atomization department takes into account the stage of mixing raw materials with water, sieving, etc...

2.6. Life cycle impact assessment methodology

The used impact assessment methodology is CML 2000 version 2.05, developed by Centre for Environmental Studies (CML), Leiden University (Netherlands) in 2001, replacing the CML 1992 method. CML-IA is a database that contains characterization factors for life cycle impact assessment (LCIA) (<https://www.universiteitleiden.nl/en/research/research-output/science/cml-ia-characterisation-factors>, n.d.). This methodology allows the following impact categories to be analyzed: Abiotic Depletion, Acidification, Eutrophication, Global Warming Potential, Ozone Layer Depletion, Human Toxicity, Freshwater Aquatic Ecotoxicity, Marine and Terrestrial Aquatic Ecotoxicity, and Photochemical Oxidation. The validity of the results is global in scope, but the Acidification and Photochemical Oxidation categories are based on average values for the European region (De Bruijn et al., 2002).

This methodology provides information on human health, natural resources and the environment and has been used in numerous works in the literature (Ibáñez-Forés et al., 2013; Özkan et al., 2016; Muñoz et al., 2018; Uceda-Rodríguez et al., 1917). The evaluation of impact indices against an average European in one year is standardized.

The software SimaPro 8.3.0.0 (PRé Consultants) enabled the model construction and data processing.

3. Results and discussion

Fig. 3 shows the impacts associated with total tile production (m^2) compared to the year 2022. For each impact category and scenario, the comparison of total inputs and raw material transportation inputs can be seen.

It is evident that over 95 % of the impacts are from the transportation of raw materials from quarries to the manufacturing site; this is even more evident in Table 1. As mentioned in Section 2.3, impacts related to raw material extraction, transportation and manufacturing were considered for each scenario. Table 1 shows the percentage influence of each analyzed phase on the related impacts.

Ibáñez-Forés et al. (2013), in a 2013 paper on tile production in Spain, observed that recovering heat from the production cycle can achieve environmental improvements of more than 90 %. In this case study, combined heat and power (CHP) significantly reduced the impact of manufacturing, as shown in Table 1. Ceramic companies are energy-intensive companies; in fact, if combined heat and power were not considered, most likely the production phase would be the most impactful in agreement with other studies (Almeida et al., 2016; Ibáñez-Forés et al., 2013).

In all cases, the pumice and lapillus scenarios show a decrease from the reference. The categories that show a greater decrease in impacts are “Acidification” and “Photochemical oxidation” while those that are close to the values of the reference scenario are “Freshwater aquatic ecotoxicity” and “Marine aquatic ecotoxicity”. Although the relative improvement is less evident, the absolute decrease in “Marine aquatic ecotoxicity” and “Freshwater aquatic ecotoxicity” is still relevant, as they are in the order of E12 kg 1,4 DB eq and E9 kg 1,4 DB eq respectively.

In all scenarios, the greatest impacts occur in the categories “Marine aquatic ecotoxicity”, “Human toxicity”, “Fresh water aquatic ecotoxicity,” and “Global warming.”

From a comparison between the pumice-based and lapillus-based scenarios, it is possible to say that the differences are very small. Nonetheless, pumice-based products have slightly lower impacts in most indicators. Probably the difference between the pumice-based and lapillus-based scenarios is due to the variation in the percentages of raw materials required to obtain the ceramic piece.

The impact of transportation is very high. According to literature data (Waterkemper Vieira et al., 2023; Almeida et al., 2016; Ma et al., 2022) transportation is very impactful and therefore these data could be confirmed, although normally the greatest impacts are related to production. In the case study, however, the model did not consider the real quantity of energy needed to produce the amount of porcelain stoneware manufactured by the company in 2022. This is due to the presence of a cogeneration plant capable of producing almost all the needed energy, so the company is self-powered. On the other hand, there are raw materials that travel over 8000 km to get to their destination.

Fig. 4 shows only the data on raw material impacts. This is to better highlight the difference between the three scenarios. In the previous figures, there is no contribution related to raw materials or production because they are negligible compared to transportation, as evident in Table 1.

The categories “Freshwater aquatic ecotoxicity” and “Photochemical oxidation” do not show a clear change from the life cycle of the reference sample. The trend in data for raw materials alone is comparable to the total data (raw materials, transport and production): there is a decrease in all categories in the case of pumice-based and lapillus-based products. Comparison of the pumice-based and lapillus-based scenarios shows that the latter scenario showed indicators with slightly lower impacts except for the case of “Fresh water aquatic ecotoxicity”.

There has been a conscious focus on transportation and raw

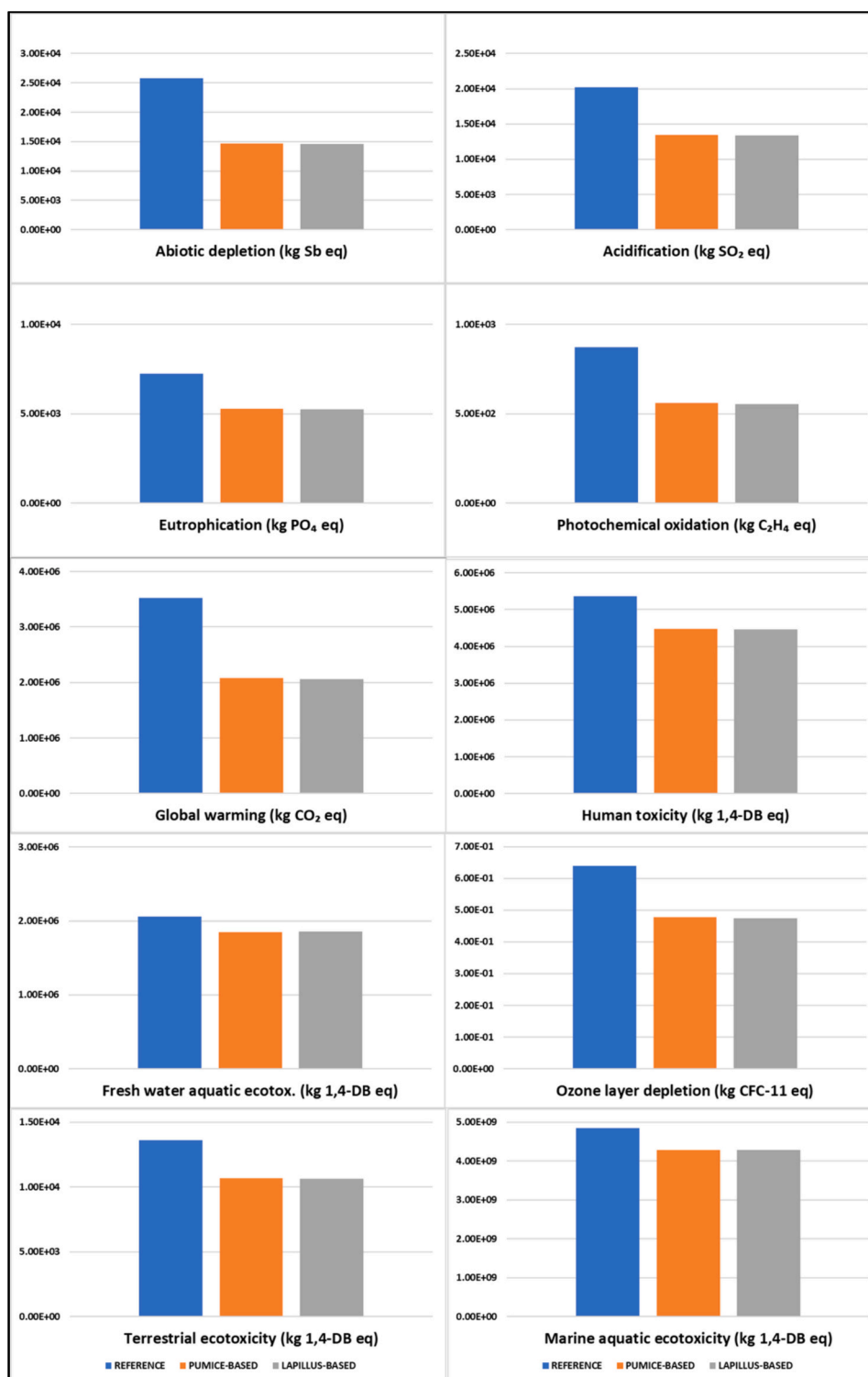


Fig. 4. Raw materials impacts.

materials, as these are the life cycle stages that vary from one product to another. One point should be made: the number of raw materials in the pumice-based and lapillus-based scenarios is significantly reduced when compared with the reference. Consequently, impacts are reduced. However, they remain very high because many of the raw materials in the reference scenario travel by rail and sea, while Italian raw materials travel by road. Hence, most of the transportation means used in the reference case are less impactful than those used in the other two cases. If we shift our attention to energy consumption, it is possible to see

that it is very low. Normally most of the impacts are due to the production process, as shown by other authors (Frischknecht and Rebitzer, 2005). In the case under study, the company works in cogeneration, recovering heat and producing electricity, avoiding buying electricity from fossil sources. Energy consumption generates somewhat higher impacts than those generated by raw materials but manages to be limited.

Fig. 5 shows the avoided impacts in the two alternative scenarios compared to the reference. The data refer to the tons of impacts avoided



Fig. 5. Avoided impacts.

in the corresponding categories.

The two scenarios are very similar to each other. As mentioned earlier, pumice waste-based tile production has slightly lower impacts in most categories, and this results in a higher percentage of avoided impacts. There are environmental benefits in each category. The categories that had less environmental benefits were “Fresh water aquatic ecotoxicity” and “Marine aquatic ecotoxicity”. The greatest environmental benefits, with a net decrease in impacts, were in the categories “Acidification” and “Photochemical oxidation.” The other categories showed improvements between about 11 % and 20 %. The obtained environmental benefits are in the range of about 20 % in both scenarios.

4. Conclusions

In this work, the life cycle of three products was analyzed: a reference product (which is a porcelain stoneware tile currently on the market), a porcelain stoneware tile containing pumice scraps, and a porcelain stoneware tile containing volcanic lapillus scraps. The inventory analysis made it possible to evaluate the impacts deriving from the extraction and transportation of raw materials and from product manufacturing. Impact categories were evaluated with a focus on raw materials and their transportation, as they differentiated one scenario from another. The manufacturing process remained the same in all three scenarios.

It was observed that:

- For each scenario, transportation is responsible for more than 95 % of the generated impacts, followed by the production process and finally by the raw material extraction process, which only in one case generated impacts greater than 0.2 %;
- In the two scenarios in which volcanic scraps were among the raw materials, the impacts decreased in any analyzed category;
- The reduction in impacts ranges from a minimum of about 8 % in the “Fresh water aquatic ecotoxicity” and “Marine aquatic ecotoxicity” categories, to a maximum of about 48 % in the “Acidification” category;

- The influence of transportation is still high in the two proposed case studies, because:

- notwithstanding the raw materials come from Italy, they travel mainly by road, with a corresponding high impact;
- the impact associated with energy consumption is low because the factory is almost energy self-consistent, so the impact produced by the transportation is emphasized.

Impacts could be further reduced by:

- evaluating more environmentally friendly means of transportation, as Italian raw materials currently travel by road. It would be better if they traveled by train;
- evaluating raw materials located close to the production site.

It was very difficult to compare the present study with others in the literature. Points of agreement were found, such as the high impact of transportation, and others in disagreement, such as the impacts generated by manufacturing. Working with a specific plant and at an industrial level has the advantage of being at an advanced stage of scale-up; on the other hand, there are limitations due to the inherent nature of the considered plant, in particular the cogeneration aspect, which greatly reduces the impact of the manufacturing phase. In any case, it is still possible to state that pumice and lapillus-based tiles, in addition to having good technological performance, are more environmentally and human health friendly than the considered reference. Although the impacts can be further reduced, the obtained results strengthen the importance of using these types of scraps for the production of porcelain stoneware.

CRediT authorship contribution statement

F. Altimari: Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis. **F. Andreola:** Writing – review & editing. **I. Lancellotti:** Writing – review & editing, Conceptualization. **L. Barbieri:** Writing – review & editing, Conceptualization.

Teresa Cotes-Palomino: Writing – review & editing, Supervision, Resources, Conceptualization. **Carmen Martínez-García:** Writing – review & editing, Resources, Conceptualization. **Manuel Uceda-Rodríguez:** Investigation, Formal analysis. **Ana Belen López-García:** Writing – review & editing, Validation, Supervision, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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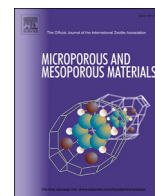
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From quarry by-products to a zeolites-based Zn fertilizer with increased resistance to rain leaching

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ABSTRACT

In the face of an extensive literature on the use of zeolites for the removal of metals from water for environmental purposes, it is seldom considered that some metals are also essential nutrients for life and that zeolites could be profitably used to dose their release. Among these, Zn is a key micronutrient, and when its demand by crop is not fully balanced by adequate accessibility, fertilization must be provided using Zn salts that can be, however, easily leached and partly wasted in the environment.

In an attempt to solve this critical problem, a new controlled-release formulation of Zn using zeolite-containing geomaterials was designed, prepared, characterized, and tested by applying a sequential, multi-method approach. Different formulations were trialed, and the most effective included 30 wt% pumice by-product and 70 wt% clinoptilolite-rich zeolitized tuff, with about 20 mg/g of exchangeable Zn²⁺. The enrichment process reached equilibrium after about 8 h, a timing well-tuned with technology transfer. Desorption kinetic tests in a weekly acid environment revealed gradual Zn release, with about 4.28 wt% released after 6 h. When tested as a foliar fertilizer on *Vitis vinifera*, this formulation demonstrated superior resistance to leaching under simulated rainfall conditions compared to conventional ZnSO₄·6H₂O fertilizer, maintaining the initial level of Zn (130 mg/kg of dry leaves), while about 22 % of the Zn applied with ZnSO₄·6H₂O was lost. This outcome was plausibly due to mineral particle adhesion to leaf. Preliminary cost estimates suggest that the product designed here can be placed in the market with competitive sales prices.

1. Introduction

To supply fertilizers to the aerial part of plants, the use of cation-exchanging microporous materials could be a viable option [1–6]. Among them, zeolites are very promising geomaterials [7–11]. In fact, zeolites are characterized by properties such as high and selective cation-exchange capacity (CEC), reversible hydration and molecular sieving, which give them a high agronomic value [12–14]. This success is confirmed by several studies and applications regarding their use as soil amendments [15–28], for nutrient recovery from wastewaters and livestock manure [26,29–35] and, more recently, as corroborants for foliar treatments, also due to their persistence on leaf surfaces when applied in micronized form [17,36–44].

Although recent studies show that zeolites synthesized from wastes such as fly and bottom ash can be used in a variety of application contexts [45–47], almost just volcanic tuffs are currently used in agriculture

[48]. Volcanic tuffs are rocks that may contain up to 70–80 wt% of zeolitic species such as clinoptilolite, mordenite, phillipsite and chabazite in varying amounts depending on the genetic conditions and geological history of the area. It is important to emphasize that using zeolitized tuffs in agriculture does not necessarily involve the opening of new quarries, but rather the exploitation of by-products from already existing ones. In fact, in the past (and largely even today), zeolitized tuffs were used to obtain natural stone for construction; over the years, considerable amounts of zeolite-rich scraps have accumulated (Fig. SOM-1 in Supplementary Online Material, SOM here after, in [Appendix A](#)) that can be profitably used in various large-scale applications [17,22,23,26], becoming a core business for many quarries.

On the other hand, there are more problematic quarrying by-products, such as those resulting from the mining and processing of pumices and lapilli, highly porous rocks originating from explosive volcanic events. Nevertheless, both pumice and lapillus, like tuffs, may

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contain nonnegligible amounts of zeolitic species (up to 15 wt%), possibly making these geomaterials effective cation exchangers. Unfortunately, according to regulations currently in force in Italy [49], and indirectly applied in other nations as well, only geomaterials that contain at least 50 wt% of zeolitic species, whether or not they are by-products, can be classified and traded as soil improvers, which are the major source of consumption of these by-products in agriculture. Therefore, finding additional ways to use geomaterials with modest zeolitic content is undoubtedly a timely challenge, with not only environmental, but also managerial and economic implications, considering that the mining sector produces more than 100 billion tons of solid waste per year globally [50].

In the face of numerous studies involving zeolites in Zn removal for various environmental application, only very few researches have considered them as an efficient geomaterial for Zn fertilization in soil or plant leaves [51] or to modelling the heavy metals, including Zn, mobility in zeolite-amended soils, with implication also on their bioavailability [52,53]. Zn is a fundamental micronutrient for humans, being responsible of catalytic, structural and regulatory functions in mammals [54]. About 33 % of the Zn ingested is effectively absorbed in the small intestine, where it is then transported to the liver, and finally to other tissues via the systemic circulation [55]. Cellular Zn pools are then regulated by the influx or release from intracellular stores of Zn or supplied by either metallothioneins (proteins that bind Zn and act as an intracellular reservoir), or heavy-metal ATPases (enzymes that control Zn in cytosol using the energy of adenosine triphosphate) [56]. The importance of Zn for human body is evidenced by the many roles of Zn finger proteins, that control the expression of growth-related genes, immune response mediators, and steroid receptors [57]. Despite this, Zn deficiency is a growing threat, especially in poor and developing countries, often resulting in increased susceptibility to infections, reduced physical power, growth retardation, as well as neurobehavioral impairments in children [58–61]. The main reasons for low dietary intake are poor levels of bioaccessible Zn in agricultural soils (about 50 % show inadequate levels of Zn) and non-diversified diets based on cereals and cereal-based products [62–64]. The latter, is indeed a common feature inherited from earliest days of agriculture, around 9 K-years ago, when only a few species of cereals (wheat, rice and maize) were selected for cultivation [65]. Because Zn, as well as other essential micronutrients, increase its concentration within specific trophic levels along terrestrial food webs (biomagnification), significantly higher levels of Zn are present in animal products and meat than in cereals [66]; consequently, low or null consumption of meat in developing countries is among the causes of Zn deficiencies and related pathological disorders [60].

Beyond this, there are other aspects not strictly related to food safety and accessibility, but still relevant to the economies of many countries. In fact, an adequate supply of Zn is also crucial in horticulture and viticulture, as it contributes to plant health [67–70]. For plants, Zn is an essential component of Zn-binding proteins with structural functions. It is involved in transcription, translation, photosynthesis, and the metabolism of reactive oxygen species [71]. Zn is also important for plant–pathogen and pest interactions [72]. Indeed, increased levels have been associated with heightened immune system response and resistance to pathogenic infections, while deficiencies have been related with increase susceptibility to fungal diseases [73,74]. Deficiency symptoms include chlorosis, reduced growth and yield, and reduced micronutrients in cereals grains [71]. Radial transport of Zn to the xylem (and thus to the shoots) occurs through two main pathways, namely the symplastic and apoplastic. The former transports Zn (as well as sugars and other molecules) between cells within the cytoplasmic continuum of root cells, the latter through extracellular spaces called apoplasts, where specific barriers (e.g., the Casparian stripe) serve to control nutrient fluxes [71,75]. In all cases, the presence of Zn in bioavailable form is critical.

Stimulating Zn bioaccumulation in plants (biofortification) could be a valid response in contexts where crop demands for Zn is not fully

balanced by adequate Zn accessibility from the soil [76–80]. Nevertheless, the efficacy of Zn fertilization in soils is often limited by several reasons, including, the high solubility and rapid leaching of mineral Zn fertilizers, the possible sequestration through cation exchange reactions with clay minerals and the soil organic matter (formation of non-bioavailable organometallic complexes), and limited translocation from root systems to edible parts of plants [81–89]. In addition, its mobility can be affected, although to a lesser extent than other metals, just by soil amendment actions with zeolites [52] or other organic and inorganic amendments [90]. For these reasons, Zn foliar application has gained momentum as an alternative or supplementary strategy to soil application [91–93]. Moreover, particularly promising scientific outcomes [94–96] recently demonstrated with ^{65}Zn isotopic tracing, efficient translocation of Zn from wheat leaves to grains, further validating foliar fertilization as a preferential technique. The choice of one or the other strategy should be however weighed against the site-specific characteristics of the soil [89], the crop [76,80,97], and the type of Zn-based fertilizer [98].

Based on these premises, this research aims to prepare a new controlled-release Zn foliar fertilizer [99] composed of a mixture of zeolites-containing quarry by-products with the purpose of reducing environmental impacts and quarry costs. This formulation should release Zn gradually over a longer period than a conventional fertilizer and, therefore, provide plants with a steady and sustained supply of Zn for growth while minimizing nutrient loss through leaching. The possible occurrence of different zeolitic species in the various geomaterials used, could also provide advantages in terms of differential release of Zn (i.e., kinetic), as each zeolitic species reacts differently depending on its crystal chemistry [100–102]. More specifically, Zn adsorption and desorption and cations diffusivity were investigated in mixtures with varying amount of a clinoptilolite-rich zeolitized tuff, pumice and lapillus scraps. The most promising formulation was then tested as foliar fertilizer on *Vitis vinifera* to evaluate its resistance to simulated rain leaching with respect to a commonly used Zn fertilizer ($\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$). A preliminary cost-benefit analysis was performed as well.

2. Instruments, materials and methods

2.1. Analytical instruments

Geomaterials were characterized with a consolidated multi-analytical protocol [103,104], encompassing particle size analysis, surface areas measurement with the multi-point Brunauer–Emmett–Teller (BET) method, X-ray powder diffraction (XRPD), X-ray fluorescence (XRF), scanning electron microscopy equipped with an energy dispersive X-ray detector (SEM-EDX) and elemental analyses (EA) to quantify the carbon and nitrogen contents, the latter used to calculate the CEC in the geomaterials saturated with $[\text{NH}_4]^+$. Inductively coupled plasma optical emission spectroscopy (ICP–OES) was used for measuring the dissolved cations (Zn^{2+} , Al^{3+} , Na^+ , Mg^{2+} , K^+ , Ca^{2+}) in liquid samples. Detailed description of instruments and experimental set up is reported in the SOM–1.

2.2. Geomaterials

The geomaterials used (section 3.1) are a clinoptilolite-rich zeolitized tuff (ZT), pumice (PU) and lapillus (LA) from Bono (Sassari, Sardinia, Italy), Riserva Muraccio (Tessennano, Viterbo, central Italy) and Monte Cellere (Cellere, Viterbo, central Italy) quarries, respectively. The analytical methods employed for their characterization are described in SOM–1 and SOM–2. More information on the properties and applications of geomaterials like those used in this study are described in the literature [105–107].

2.3. Formulations design and preparation

In the following, Zn and Zn^{2+} will be used to refer to the metal in the broad sense or the exchangeable cation, respectively. As indicated in the labels of a wide range of commercial products and also in the literature [108–110], the recommended doses of Zn for foliar applications range between 200 and 300 g/ha, depending on various factors such as soil conditions and specific nutritional requirements of crops. Therefore, a formulation containing about 20 mg of exchangeable Zn^{2+} per g of product (equivalent to 61.2 mEq of Zn^{2+} per 100 g) was foreseen. Under these conditions, the amount of product used would be about 10–15 kg/ha, paralleling the dosage usually employed in foliar treatments with natural powdered corroborants.

Based on the results after described in section 3, four different formulations were prepared, identified hereafter as $\text{ZT}^{70}\text{PU}^{30}$, $\text{ZT}^{70}\text{LA}^{30}$, $\text{ZT}^{85}\text{PU}^{15}$ and $\text{ZT}^{85}\text{LA}^{15}$ composed of 70 or 85 wt% of ZT and 30 or 15 wt % of PU or LA, respectively. Preparation was done by simultaneously grinding appropriate amounts of each geomaterial in an agate mill until a micronized powder was obtained as indicated by the particle size analyses (Figs. SOM-2-SOM-5).

2.4 The adsorption of Zn^{2+} by ZT at equilibrium and non-equilibrium conditions

The CEC of a zeolite depends not only on its crystal chemistry and exchangeable cations, but also on several other parameters, including particle size, interaction time, and the solid/solution ratio [100–102]. Therefore, once fixed the particle size, the minimum contact time required to obtain a near-equilibrium condition, and the optimum solid/solution ratio were accessed by kinetic (time dependent) and equilibrium (equilibrium concentration dependent) adsorption tests, respectively, as detailed in SOM-3. Although cation exchange may be boosted by temperature, it is still a spontaneous reaction and room temperature (20 °C) was used in this research to avoid any waste of energy.

2.5. Preparation of Zn^{2+} -enriched formulations and release tests

The four formulations ($\text{ZT}^{70}\text{PU}^{30}$, $\text{ZT}^{70}\text{LA}^{30}$, $\text{ZT}^{85}\text{PU}^{15}$ and $\text{ZT}^{85}\text{LA}^{15}$) were enriched in Zn^{2+} , according to the results of adsorption kinetic tests. The amount of adsorbed Zn^{2+} was checked through ICP-OES after conventional nitric-hydrofluoric digestion. Each formulation was investigated for Zn^{2+} desorption kinetic in a weakly acid environment, simulating common rain pH [111], and compared with ZT. Details about Zn^{2+} loading and desorption kinetic batches are reported in SOM-4.

2.6. Residence test on *Vitis vinifera* after a simulated rain event

$\text{ZT}^{70}\text{PU}^{30}$ formulation was selected as the most promising option (see section 3.4 for details) and therefore further investigated as foliar treatment on *Vitis vinifera* (Trebbiano Romagnolo cultivar). The test was performed by a professional agronomist in a greenhouse (Valsamoggia, Bologna, north Italy) and included a positive control (plant fertilized with $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$, as conventional fertilizer) and a negative one (no treatment) to assess background Zn. Briefly, more details are given in SOM-5, 15 plants were sprayed, 5 with the formulation ($\text{ZT}^{70}\text{PU}^{30}$), 5 with $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ solution (positive control) and 5 with tap water (control). Each plant received 3 treatments, each 48 h apart, which provided, a total of 20 mg Zn per plant (regardless of the source of the metal, i.e., the $\text{ZT}^{70}\text{PU}^{30}$ or $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$). The aim was to verify the persistence of Zn (both bioaccessible and its total amounts) on the leaves, before and after a simulated rain event. To achieve this information, sequential extractions were applied (SOM-5). The leachable fraction was evaluated in water extracts, while the fraction resistant to the leaching was measured in subsequent extracts of concentrated HNO_3 . The former for the purpose of measuring leachable Zn from rain,

the latter the Zn absorbed by leaves or present in the formulation remaining on the leaves. A further check followed a more conventional procedure by analysing total Zn in leaves ash.

Significant differences ($p < 0.05$) were obtained with ANOVA and Tukey's HSD tests, that were used for normally distributed, homoscedastic populations (as resulted from Shapiro–Wilk and Bartlett's tests), whereas Kruskal–Wallis was used for non-normally distributed, non-homoscedastic data. Statistical analyses were performed with R Studio [112], using MASS [113] and Agricolae [114] packages.

3. Results and discussion

3.1. Geomaterials characterization

The XRPD pattern of the considered geomaterials are reported in Fig. 1. From a strictly qualitative point of view, XRPD results indicate that mica/illite, plagioclase, quartz and sanidine are present in all samples in varying amounts.

ZT is characterized by a significantly high amount of clinoptilolite (Table 1), with Na^+ , Ca^{2+} and Mg^{2+} as the main exchange cations, as suggested by CEC and chemical analyses (Table 1, Section 3.3). Chabazite and analcime are the zeolitic species found in PU and LA, respectively (Table 1), but in lower amounts than in ZT, in accordance with the lower CEC of these two geomaterials (Table 1), a parameter closely related to the amount of zeolitic species. Hematite and pyroxene are also present in LA, in agreement with the higher Fe and Mg content in this sample compared to ZT and PU. All samples are also characterized by a significant presence of undetectable material in X diffraction (likely

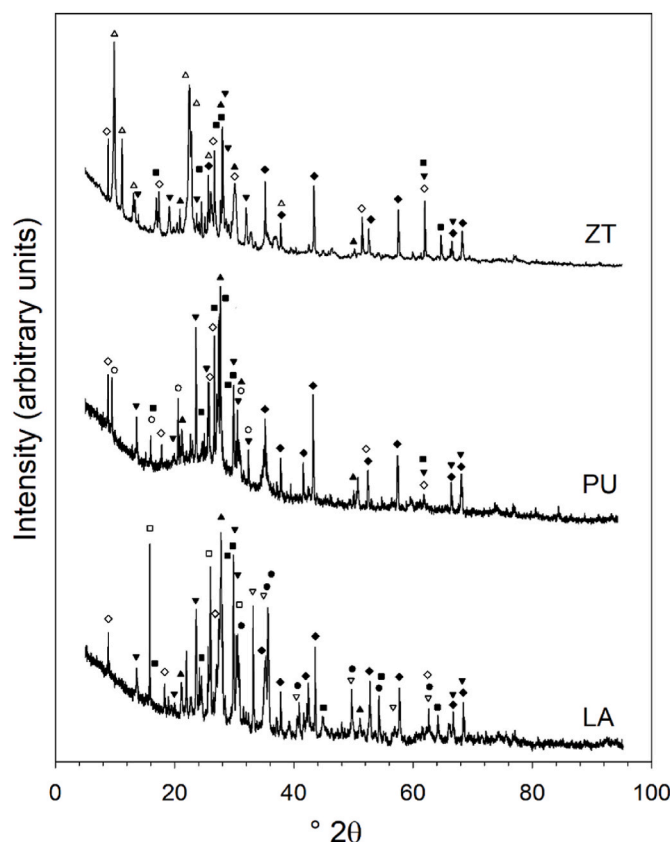


Fig. 1. XRPD patterns of ZT, PU and LA. Symbols identify the main peaks of the detected phases (Table 1) and of the internal standard NIST SRM 676a (alumina powder, corundum structure – see SOM 1.1). Open symbols: square, analcime; circle, chabazite; triangle up, clinoptilolite; triangle down, hematite, diamond, mica/illite. Filled symbols: square, plagioclase; circle, pyroxene; triangle up, quartz; triangle down, sanidine, diamond, corundum (standard).

amorphous), however, typical of geomaterials such as these originating from explosive volcanic events. This feature is also well evidenced by the increase in background signal [115] that is observed for all samples between about 20 and 30 °2θ (Fig. 1); in fact, this increase is best evident in the PU sample, which is the one characterized by the greatest amount of amorphous (Table 1).

In agreement with its mineralogical composition (about 64 wt% of clinoptilolite) and as found for other similar geomaterials (clinoptilolite-rich tuffs) recently described in the literature [118–122] ZT has a specific surface area of $22.838 \pm 0.238 \text{ m}^2/\text{g}$. This value is close to that of PU ($18.005 \pm 0.099 \text{ m}^2/\text{g}$) and significantly higher than that of LA ($2.106 \pm 0.023 \text{ m}^2/\text{g}$). Although zeolitic tuffs generally have a slightly higher surface area than pumices due to their crystalline and microporous structure, a direct comparison between these different materials is not possible because of the different geological context of origin and the different processing undergone [123].

3.2. Characterization of Zn^{2+} adsorption by the ZT

The Zn^{2+} adsorption equilibrium test on ZT (see SOM–3.1 for experimental detail) showed a peculiar C_e – q_e plot, where C_e (equilibrium concentration of Zn^{2+} in solution, mg/L) and q_e (Zn^{2+} adsorption capacity at equilibrium, mg/g) were indirectly related (Fig. 2A). Inverse q_e to C_e trends are not possible in cation exchange, as they represent a condition where the higher the mass/volume ratio, the more exchange occur per unit mass. Nevertheless, inverse q_e to C_e correlations likely represent a system where fractions of Zn^{2+} precipitated as low soluble salt. SEM–EDX analysis (Fig. 3) carried out on ZT powder derived from batch $\geq 6 \text{ % w/v}$ (SOM 3.1) effectively revealed the occurrence of domains with significant Zn amounts, up to localized 70 wt%. Since ZT was washed several times with Milli-Q water after the exchange with Zn^{2+} , and EDX spectra (Fig. 3) did not reveal sulfur-related signals, the occurrence of residual $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ is not plausible. Considering that the tCEC of the ZT was 159 mEq/100g (Table 1), the maximum adsorbable Zn^{2+} should not exceed 5.2 wt%. Values significantly higher than 5.2 wt% (also considering the semiquantitative outreach of EDX measurements) are therefore not explainable with adsorption/exchange reactions, supporting instead the occurrence of Zn precipitate (condition

represented by red dots in Fig. 2).

Curves in Fig. 2A shows that the precipitation of Zn phases was ZT dose-dependent. The addition of zeolites to a solution can indeed apport significant differences in chemical properties, not only in terms of cation exchange, but also concerning pH. More specifically, zeolites may significantly increase the pH of soils [52] and solutions, possibly favouring the precipitation of metal oxide and hydroxide [124]. Paralleling the procedure described in SOM 3.1, a test was performed for evaluating the pH variation starting from a 0.1 M $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ solution, in contact with different doses of ZT, with solid/liquid ratios ranging from 1 to 16 % (w/v). Samples were mixed at 400 rpm in closed PVF flasks for 24 h, then pH was measured (Fig. 2B). The initial pH was 4.8, slightly lower than the theoretical value (5.0) calculated with Equation (1), considering $pK_{a1} = 9.05$ and $C(s) = 0.1 \text{ M}$ [125], because of the addition of a few drops of HNO_3 , used to facilitate the solubilization of $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$.

$$\text{pH} = 0.5pK_{a1} - 0.5 \log(C_s) \quad (1)$$

Once in contact with ZT, pH linearly increased with ZT dosage, to a maximum of 7.8 (reached at 16 % w/v). The condition that first revealed Zn precipitates in SEM–EDX analysis (6 % w/v) showed a pH of 5.8. It is therefore likely that pH change by zeolites concurred in the precipitation of Zn phases [126]. In fact, Fig. 3A shows a grain of ZT material after $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ batch, surrounded by smaller tabular or plate-shaped precipitates and the regions within red dashed lines in Fig. 3B, revealed Zn concentrations greater than 20 wt%.

3.3. Cation exchange kinetic of ZT during Zn^{2+} adsorption

Zn^{2+} adsorption kinetic measurements were performed as described in SOM–3.2. The cations released by ZT during Zn^{2+} adsorption are reported in Table 1. Equilibrium desorption capacities (q_e , measured at 28 h) for Na^+ , Ca^{2+} , K^+ and Mg^{2+} indicate an aCEC of 83.4 mEq/100g (Fig. 4A; Table 1). As expected, this value was significantly lower than the tCEC measured using $[\text{NH}_4]^+$ as the exchange cation (159 mEq/100g, Table 1) because of the lower affinity of clinoptilolite towards Zn^{2+} compared to $[\text{NH}_4]^+$ [102,127]. However, with respect to ZT, the value of 83.4 mEq/100g for Zn^{2+} largely meets the target required for a

Table 1

Mineralogical (weight %) and chemical (oxide weight %) composition of ZT, PU and LA. In the mineralogical analyses (left) the standard deviation σ_Q (values in parenthesis) of the weight percentage Q of each phase was calculated using the values obtained in the output file after the quantitative refinement by GSAS software, and the formula $\sigma_Q = \{[(\sigma_a/a)^2 + (\sigma_b/b)^2]^{1/2}\} Q$ [116], where a and b are the two variables most affecting Q values and refer, respectively, to the weight fraction of the phase and the internal standard, whereas σ_a and σ_b are their standard deviations; “Amorphous” may also include very low-amount minor phases non detected through XRPD. In chemical analysis (right) the LOI (Loss On Ignition) is the weight loss (%) at 1050 °C. CEC are reported in mEq/100g as tCEC (theoretical CEC, cations exchange with $[\text{NH}_4]^+$ and aCEC (apparent CEC, cations exchange with Zn^{2+}), both as defined in Inglezakis (2005) [117] and detailed in SOM-2. Counterions are referred to aCEC and were measured only for ZT being the main component of the formulations described in section 3.3.

	ZT	PU	LA		ZT	PU	LA
Analcime	–	–	7.5(5)	LOI	12.7	4.30	1.07
Chabazite	–	12.4(2)	–	SiO_2	64.2	60.5	49.8
Clinoptilolite	63.7(8)	–	–	Al_2O_3	12.2	17.9	17.5
Hematite	–	–	7.8(3)	Fe_2O_3	2.85	3.23	9.33
Mica/illite	2.7(2)	4.7(1)	1.8(6)	MnO	0.0821	0.143	0.140
Plagioclase	6.3(2)	3.9(2)	22.1(1)	MgO	1.47	0.946	3.47
Piroxene	–	–	14.6(9)	Na_2O	1.84	2.73	4.37
Quartz	2.0(5)	2.3(1)	0.80(7)	TiO_2	0.298	0.393	1.08
Sanidine	2.9(3)	24.7(3)	7.6(6)	K_2O	1.87	7.55	3.36
Amorphous	22.4(9)	52.1(5)	37.8(8)	P_2O_5	0.0611	0.0781	0.346
				CaO	2.38	2.42	8.99
χ^2	4.428	3.383	5.216	C	0.30	0.10	0.05
R_p	0.0550	0.0524	0.0924	tCEC	159	22.3	8.93
R_{wp}	0.0805	0.0738	0.0916	aCEC	83.4 of which:		
				Na^+	52.0		
				Ca^{2+}	15.3		
				K^+	4.55		
				Mg^{2+}	11.5		

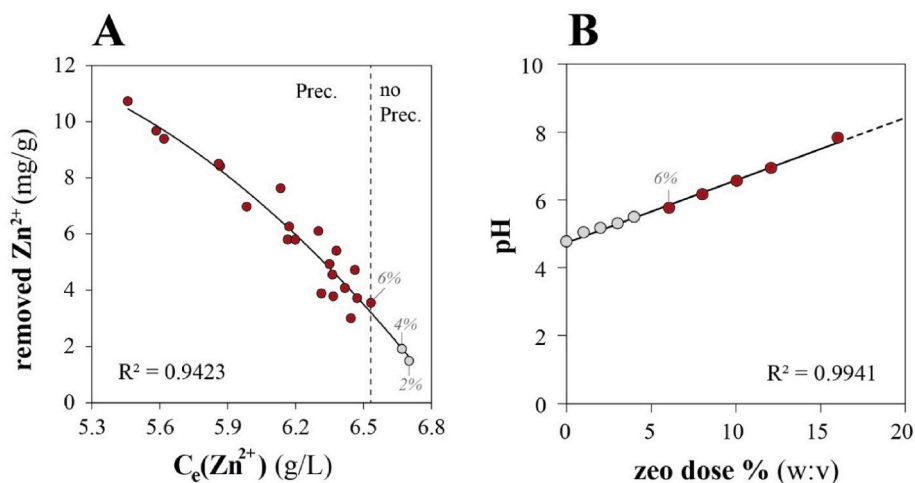


Fig. 2. Zn^{2+} adsorption equilibrium test. A) Removed Zn^{2+} at equilibrium per g of ZT, respect to residual Zn^{2+} dissolved. 2nd grade polynomial and R^2 are shown. The dotted vertical line separates the region where Zn precipitates occurred (ZT $\geq 6\%$ w/v, at the left) with the one where no precipitates have been observed (ZT $< 6\%$ w/v, at the right); B) pH effect of different w/v ratios of ZT in $ZnSO_4 \cdot 6H_2O$ 0.1M solution. Percentages (%) are intended as w/v (g of ZT/100 ml).

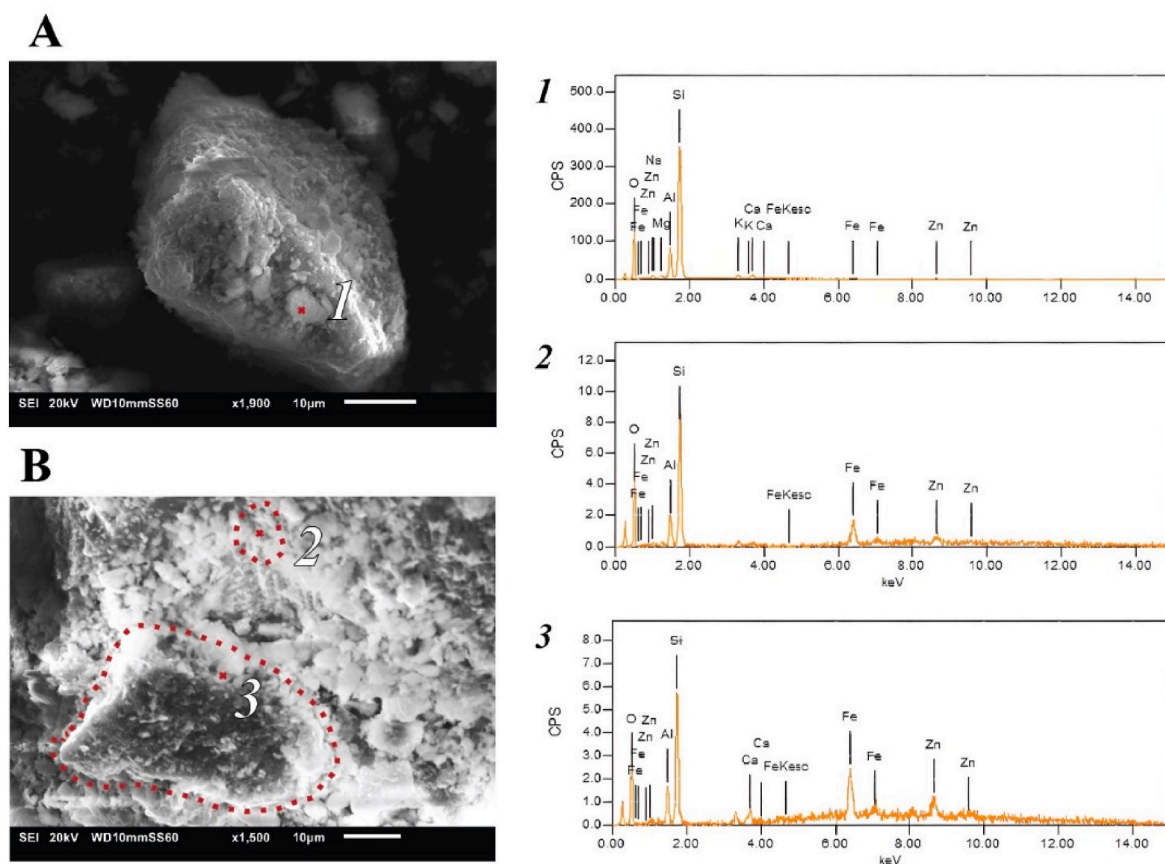


Fig. 3. SEM-EDX of the ZT treated with $ZnSO_4 \cdot 6H_2O$ 0.1M solution (at 6 % w/v batch). A) A grain surrounded by smaller tabular crystals; B) particular of a region with high Zn content (>20 wt%), highlighted by red dotted lines. On the right the EDX spectra of measurements point 1, 2 and 3 indicated in Figs. A and B.

Zn-fertilizer (61.2 mEq/100g, section 2.3).

For each measured $q(t)$ (time-dependent desorption capacities of exchangeable cations), the fractional uptake $F(t)$ was calculated as $F(t) = q(t)/q_e$ [128], where $F(t)$ represents the closeness of the system to equilibrium. Indeed, in kinetic investigations it should be avoided to use data too close to equilibrium [128], therefore, only data with $F(t) < 0.85$ were considered. The $F(t)$ values calculated for each exchangeable cation are shown in Fig. 4B. The ZT released monovalent cations (Na^+

and K^+) quicker than bivalent ones (Ca^{2+} and Mg^{2+}) as near equilibrium conditions ($F(t) \geq 0.85$) was reached for Na^+ and K^+ after about 30 min of contact, while Ca^{2+} and Mg^{2+} showed $F(t) \geq 0.85$ after about 4 h of contact. Cations with higher hydration energy, as Mg^{2+} and Ca^{2+} , present slower exchange kinetic than cations with lower hydration energy, as Na^+ and K^+ ; furthermore, zeolites with high SiO_2/Al_2O_3 ratio as clinoptilolite show increase affinity for monovalent exchangeable cations [102,127,129].

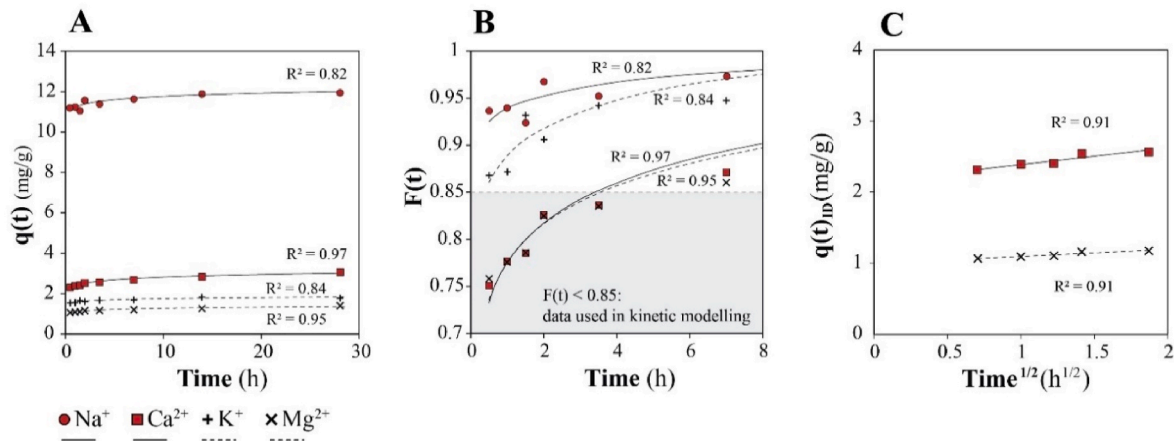


Fig. 4. Desorption kinetic of Na^+ , Ca^{2+} , K^+ and Mg^{2+} by the ZT in a $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ 0.1 M batch. A) $q(t)$ (mg/g) vs Time (h); B) $F(t)$ vs Time (h). The grey region represents $F(t) < 0.85$, therefore, the data contained were not considered in kinetic modelling. The curves in A and B are logarithmic regressions with R^2 indicated. C) Intraparticle Diffusion (ID) model for Ca^{2+} and Mg^{2+} and relative R^2 [130].

Kinetic modelling was performed for Ca^{2+} and Mg^{2+} being that only these cations provided data with $F(t) < 0.85$. The Pseudo-Second Order (PSO) [131] showed good correlation with experimental data (Equation (2)):

$$q(t) = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (2)$$

where $q(t)$ (mg/g) is the time-dependent adsorption/desorption capacity, q_e (mg/g) is the equilibrium adsorption/desorption capacity, k_2 is the PSO rate constant (g/mg h) and t is time (h). The PSO showed an optimal correlation with experimental data ($R^2 > 0.999$), however not all the assumptions were plausibly met [132], briefly: (i) adsorption is reaction-controlled, (ii) liquid concentration is constant, and (iii) no desorption occur. To exclude spurious correlations, it has been pointed out to check the distribution of standardized residuals [132] that, in this case, were not homogeneously distributed, finally confirming the inconsistency of the PSO model. Being that ZT and, particularly zeolites are microporous materials, cations diffusivity could be relevant [133]. The Weber-Morris Intraparticle diffusion model was therefore investigated (Equation (3)):

$$q(t) = k_{ID} t^{0.5} + C \quad (3)$$

where K_{ID} is the diffusion rate constant and C (mg/g) is related with the diffusivity in the boundary layer [134]. The occurrence of multiphase adsorption could be verified in the $q(t)$ vs $t^{1/2}$ plot (Fig. 4C), if multiple lines are present. In the case, the first step (line with intercept $C = 0$) represents external diffusion, followed by diffusivity-controlled adsorption [135]. Sole intraparticle diffusion occurs instead when a single line is present, intersecting the origin at $C = 0$, with K_{ID} as slope.

The intercept C is also related with the thickness of the boundary layer (physisorption), whereas monolayer condition (as the case of chemisorption and cation exchange) is related with C values near zero [134]. In this case, starting from 30 min of contact, C was 2.15 and 0.993 mg/g for Ca^{2+} and Mg^{2+} , respectively (Fig. 4C), while k_{ID} was 0.238 and 0.101 mg/g $\text{h}^{-1/2}$, suggesting that the diffusion of the exchanged species through extra-framework spaces of zeolite crystals toward the external environment did not significantly limit Zn^{2+} adsorption, at least starting from 30 min of contact, also in agreement with its surface area. The ZT is a micronized material, therefore the micropores where highly exposed to the external environment facilitating cations diffusivity both outside and inside (Zn^{2+}) the zeolitic channels. This aspect was likely particularly relevant for monovalent exchangeable cations, where the most present one (Na^+) showed an $F(t) = 0.94$ just after 30 min of contact, suggesting no significative

limitations in its diffusivity during Zn^{2+} exchange.

3.4. Zn^{2+} enrichment of the formulations and released in simulated rain water

In agreement with the assumptions outlined in section 2.3, and considering the results of sections 3.2 and 3.3, four formulations were prepared by mixing different amounts of ZT with PU and LA by-products, reducing the amount of ZT to a maximum of 30 %, therefore sufficient to ensure a CEC approximately equal to the fixed target (61.2 mEq Zn^{2+} per 100 g). The four mixtures were labelled as defined in section 2.3 and Table 2 where is also reported the amount of Zn^{2+} adsorbed after the enrichment (SOM-4).

The minor increase of Zn content in the formulations compared to the values that could be calculated from Zn-exchanged ZT (namely, -30 % ZT $\rightarrow$ 58.4 mEq/100g, and -15 % ZT $\rightarrow$ 69.5 mEq/100g) is consistent with the contribution to cation exchange of zeolites occurring in LA and, especially, PU (Table 1). Equilibrium was almost reached after 8 h, a promising timeline for technology transfer.

The interaction with simulated rain water (SOM-4) shows a gradual Zn^{2+} release (Fig. 5) for all the formulations; the total amounts of metal released remained low even after a contact time of 6 h (Table 2). The initial fast release recorded at 30 min was plausibly due to exchange process occurred in the outermost part of the zeolitic channels, that was also facilitated by the reduced grain size. This peak is more pronounced (higher release) in the $\text{ZT}^{70}\text{PU}^{30}$ formulation, even compared to the pure ZT, plausibly related to the presence in PU of chabazite (Table 1) which has higher CEC and faster release than clinoptilolite [15,136,137], the zeolitic specie occurring in ZT, rather than their surface area presenting similar values. The chabazite contained in PU (i.e., in the $\text{ZT}^{70}\text{PU}^{30}$ formulation) therefore increased the initial release rate of Zn^{2+} ; subsequently, at higher times the release curves of $\text{ZT}^{70}\text{PU}^{30}$ and ZT tend to converge, due to the higher abundance of zeolite (and exchangeable Zn^{2+}) in ZT than $\text{ZT}^{70}\text{PU}^{30}$. Similar considerations apply also to

Table 2

Zn^{2+} contained in enriched formulations (left) and percentages released after 6 h of contact with acidified water (HNO_3 , pH 5.5) to simulate rain water (right). Data for pure ZT (label ZT^{100}) are also reported for ease of comparison.

	mg/g (mEq/100g)	Release 6h (%)
$\text{ZT}^{70}\text{PU}^{30}$	19.86 (60.8)	4.28
$\text{ZT}^{70}\text{LA}^{30}$	20.16 (61.7)	1.63
$\text{ZT}^{85}\text{PU}^{15}$	23.00 (70.4)	2.26
$\text{ZT}^{85}\text{LA}^{15}$	22.70 (69.5)	1.85
ZT^{100}	26.71 (81.7)	3.07

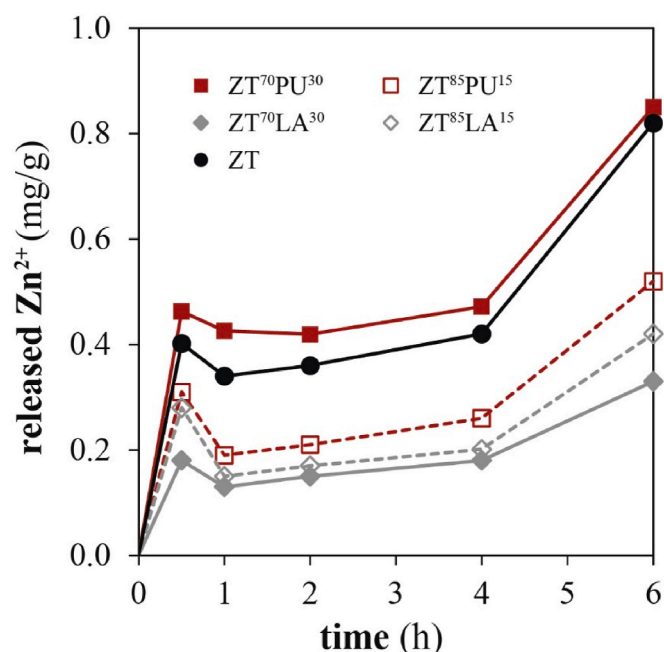


Fig. 5. Release kinetic of the formulation $ZT^{70}PU^{30}$, $ZT^{70}LA^{30}$, $ZT^{85}PU^{15}$ and $ZT^{85}LA^{15}$ compared to pure ZT.

$ZT^{85}PU^{15}$ and $ZT^{85}LA^{15}$, although the difference is less pronounced due to the higher amount of zeolite (clinoptilolite) compared to $ZT^{70}PU^{30}$. $ZT^{70}LA^{30}$ shows instead slower kinetics and lower release due to lower zeolite content, as the LA provided only minor amounts of analcime and also has a smaller surface area than ZT, which could limit cation diffusivity. For all the treatments, between 30 and 60 min the released Zn^{2+}

slightly dropped, indicating that re-adsorption and/or precipitation occurred, however, Zn^{2+} continue to be slowly released over time.

3.5. Residence of $ZT^{70}PU^{30}$ formulation on plant leaves following simulated rain event

For the reasons given in section 3.4, $ZT^{70}PU^{30}$ was considered the most suitable formulation among the four tested. Therefore, it was used to perform residence tests on *Vitis vinifera* leaves, in comparison with conventional $ZnSO_4 \cdot 6H_2O$ foliar fertilizer (see sections 2.6 and SOM-5 for further details).

The amount of Zn in the negative control was significantly lower (about -87 % less) than in the treated leaves and, as expected, no substantial differences were observed before and after the simulated rain.

Before the rain event (PRE rain columns in Fig. 6A), regarding total Zn, no differences were observed in the leaves treated with $ZT^{70}PU^{30}$ or $ZnSO_4 \cdot 6H_2O$ fertilizer, as leaves were sprayed with the same amounts of Zn (SOM-5); significant higher amount of soluble Zn was recorded in leaves treated with $ZnSO_4 \cdot 6H_2O$ compared to those treated with $ZT^{70}PU^{30}$ (PRE rain columns in Fig. 6B), which is possibly indicative of faster availability to the plant. On the other hand, $ZT^{70}PU^{30}$ showed a significantly better tolerance to the rain leaching, as evidenced by the higher Zn residuality, both total and soluble forms (POST rain columns in Fig. 6A and B, compared to $ZnSO_4 \cdot 6H_2O$). This positive effect is plausibly due to the role of active ZT and PU particles, i.e., zeolitic species, in enhancing the permanence of Zn on leaves compared to the more mobile $ZnSO_4 \cdot 6H_2O$. The increased persistence is also correlated to the physical interaction between lithoid particles of the formulation and the rough morphology of the leaf surface, which facilitates its adhesion, a feature already observed in plants treated with natural zeolitized tuffs [138]. In other word, $ZT^{70}PU^{30}$ not only act as a carrier for Zn, but also as a holder for its residence on leaves.

Being zeolites aluminosilicates, the Zn/Al ratio could be indicative of

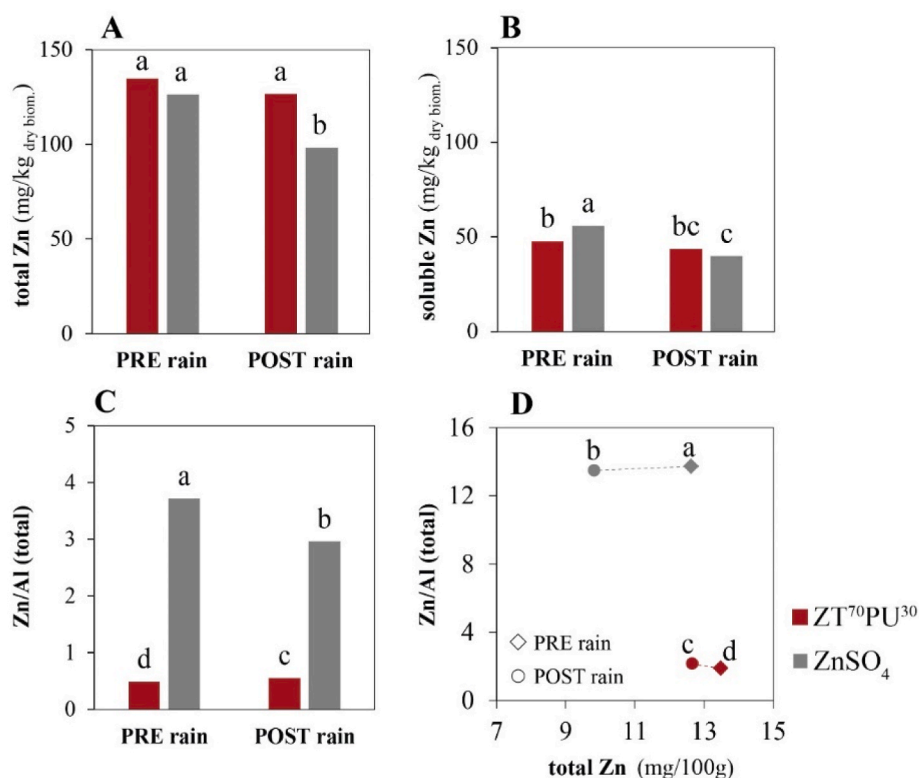


Fig. 6. Zn concentration on leaves and residence time before and after a simulated rain event. A) total Zn (mg/kg dry biomass); B) soluble Zn; C) Zn/Al ratio; D) total Zn vs Zn/Al plot. Two conditions are significantly different if no letter (i.e., a, b, c, d) is in common, as resulted from ANOVA and Tukey's HSD tests.

the permanence of $ZT^{70}PU^{30}$ on plant leaves (Fig. 6C and D). Indeed, the Zn/Al ratio decreases in $ZnSO_4 \cdot 6H_2O$ treated leaves after the rain event, whereas in $ZT^{70}PU^{30}$ it significantly increased, suggesting that the rain event did not much affect the persistence of mineral particles on leaves (Fig. 6C), and the capacity of zeolites in providing Zn in bioaccessible form (Zn^{2+}) was maintained more efficiently than with conventional $ZnSO_4 \cdot 6H_2O$ (Fig. 6D).

3.6. Preliminary cost outlook

Reimplementing PU and LA by-products is generally limited by their small grain size (often <3 mm). In addition, both are marked by very high operating costs, up to 1.20 €/m³. Therefore, PU and LA by-products are mostly reused for quarry restoration, with additional costs for transportation. Alternatively, according to current Italian [139,140] and European [141] laws, quarry by-products can be stored in areas within the quarry's jurisdiction, authorized as internal landfills, and a fee must be paid if they are resold.

Although there are no industrial plants dedicated to produce the $ZT^{70}PU^{30}$, an estimate of the production cost could be obtained considering the cost of producing atomized mixtures in ceramic tile industry. The latter materials, in fact, are produced using wet grinding plants into which any geomaterial (including zeolitized tuffs) can be placed in addition to water and a soluble salt (in this case, $ZnSO_4 \cdot 6H_2O$). Given current energy and material costs, the production of a formulation consisting of 100 % ZT exchanged with Zn^{2+} is estimated at about 2.70 €/kg (± 0.25 €/kg depending on the production capacity of the grinding plant). Replacing up to 30 wt% of ZT with PU ($ZT^{70}PU^{30}$) would result in savings of about 5 % of the total, but without considering the environmental benefit and fees no longer due for storage of PU by-product. These estimates, although preliminary, would allow $ZT^{70}PU^{30}$ to be placed in the current market with sale prices similar, or even lower, to those of other conventional Zn fertilizers.

4. Conclusions

Zn plant deficiency relates with plant disease, human dietary deficit and health issues. Therefore, providing Zn to crops in case of inadequate plant uptake from the soil is necessary. Zn fertilizers are however generally associated with low efficiency. A new foliar fertilizer formulation based on natural geomaterials rich in zeolites was proposed here, with the aim of meeting both the demand for efficient Zn-based plant nutrition and the disposal of problematic quarry by-products.

The best formulation, with unreduced properties respect to pure ZT, comprised 70 wt% of ZT and 30 wt% of pumice scraps. This formulation, for the same amount of Zn used, sprayed on plant of *Vitis vinifera* showed slower releasing properties and significative adhesion on leaves, proving better residence than traditional $ZnSO_4 \cdot 6H_2O$ fertilizer to rain leaching.

From the perspective of economic viability, net of environmental benefits, preliminary cost estimates suggest that $ZT^{70}PU^{30}$ can be placed in the market with competitive sales prices. Although possibly side effects are expected to be less than those experienced with conventional fertilizers, medium-to-large-scale agronomic assays will be needed before trade to demonstrate its true efficacy, absence of phytotoxicity and medium- and long-term impacts on (micro)organisms. Similarly, a comparison with other slow-release foliar fertilizers (e.g., coated/encapsulated/chelated Zn compounds) is necessary both in terms of efficacy and cost-effectiveness.

Assuming an ever-increasing demand for Zn-based fertilizers, the development of methodologies for recovering and reusing Zn from wastewater could be an additional challenge for circularity which could nicely match with the outcome of this research.

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CRediT authorship contribution statement

Galamini Giulio: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Daniele Malferrari:** Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Altimari Fabiana:** Writing – original draft, Validation, Resources, Methodology, Investigation. **Orlandi Silvia:** Writing – original draft, Validation, Resources, Methodology, Investigation. **Barbieri Luisa:** Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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