

Experimental Characterization of Moroccan Phosphate By-Products in Cementitious Mixtures for Potential 3D Concrete Printing Applications

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Research Article

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Abstract

This study investigates the valorization of Moroccan phosphate-industry by-products from OCP in cementitious mixtures for potential 3D concrete printing applications. The research focuses on incorporating phosphate waste materials, including waste rock, phosphogypsum (PG), and sludge, into cement-based formulations containing crushed sand and red clay. The experimental program evaluates the mechanical and rheological properties of mixtures prepared using different proportions of phosphate by-products and three cement types, designated C25, C45, and C65 in the original experimental program. The influence of mixture composition, water content, and constituent materials on compressive strength and rheological behavior was examined, with results compared against cast reference specimens. The maximum reported compressive strengths were 21.877 MPa, 32.123 MPa, and 46,528 MPa for mixtures prepared with C25, C45, and C65 cement, respectively. The results indicate that the mechanical performance of the developed mixtures depends on the cement type and the proportions of the constituent materials. Although the observed mechanical and rheological properties suggest potential for further development, the suitability of these formulations for extrusion-based 3D concrete printing remains to be experimentally validated. This study provides an experimental basis for investigating the incorporation of Moroccan phosphate-industry by-products into cementitious materials and supports further research into their potential use in sustainable construction. Future work should address direct printing trials, interlayer bonding, buildability, environmental performance, and the environmental safety of the resulting materials.

Keywords: Phosphate-industry by-products; cementitious mixtures; mechanical characterization; rheological properties; circular economy; waste valorization.

1. Introduction

OCP SA is a world leader in the phosphate and phosphate derivatives market. The company extracts, processes, and markets phosphate rock, phosphoric acid, and fertilizers. OCP SA is the world's leading exporter of phosphate rock and phosphoric acid and one of the largest fertilizer producers. Its customer portfolio includes more than 150 companies across five continents. In Morocco, OCP's industrial activities include phosphate extraction and processing plants, chemical plants producing phosphoric acid and fertilizers, and ports dedicated to exporting finished products and importing raw materials [1]. Moroccan phosphate rock is characterized by a complex mineralogical and geochemical composition. It mainly consists of apatite (phosphate mineral), silica, carbonates (calcite and dolomite), clays, and organic matter. In addition, Moroccan phosphates contain major elements such as P_2O_5 , mineral and organic carbon, fluorine, magnesium, calcium, and sulfur, as well as trace elements including uranium, thorium, rare earth elements, and heavy metals such as cadmium and zinc [2]. Sedimentary phosphate rocks, also known as phosphorites, are sedimentary formations rich in phosphate minerals, mainly belonging to the apatite group, particularly carbonate-fluorapatite. Their formation is associated with marine biological activity, chemical precipitation, and early diagenetic processes [2]. The valorization of mining waste has attracted increasing attention worldwide due to the environmental impacts associated with waste storage and the need to develop sustainable resource management strategies. In particular, phosphate mining generates large quantities of waste materials, including waste rock, phosphogypsum (PG), and phosphate sludge. These residues remain largely underutilized despite their potential for industrial applications [3,4]. Previous studies have investigated the valorization of phosphate mine waste rocks and sludge, highlighting both the challenges and opportunities associated with their reuse in construction materials [3]. Moreover, phosphate mine waste rocks have been explored as alternative materials for construction applications, demonstrating promising potential for reducing environmental impacts and promoting circular economy approaches [4]. Additive manufacturing (3D printing) has emerged as an innovative technology with successful applications in several industrial sectors, including aerospace, automotive, healthcare, and construction [5 – 7]. In the construction field, 3D concrete printing (3DCP) has received increasing interest due to its ability to automate construction processes, reduce material consumption, and enable the fabrication of complex geometries. The first investigations into construction-

scale 3D printing were reported by Pegna [5], and since then, research activities in this field have grown significantly. Several studies have analyzed the advantages, challenges, and limitations associated with the implementation of 3D printing technologies in construction. The main advantages include reduced construction time, lower labor requirements, reduced material waste, and greater design flexibility [6,7]. Furthermore, 3D concrete printing is considered a promising approach for sustainable construction due to its compatibility with low-environmental-impact materials and waste-based resources [7–10]. The most commonly used material for 3D concrete printing is Portland cement-based concrete [11]. However, the high environmental impact associated with cement production, particularly CO₂ emissions, has encouraged researchers to investigate alternative cementitious binders with lower environmental footprints [12]. Several alternative materials have been studied for 3D printing applications, including geopolymers, magnesium oxide (MgO)-based cements, aluminate cements, limestone and calcined clay-based cements, and gypsum-based materials [12,13]. Geopolymer-based materials have attracted considerable attention due to their potential as sustainable alternatives to Portland cement. Their specific properties, including relatively high mechanical strength, low environmental impact, and compatibility with additive manufacturing processes, make them promising candidates for 3D printing applications [9,10]. However, several challenges remain, including controlling rheological behavior, setting time, and printability parameters [10]. Magnesium-based cementitious materials have also been investigated for extrusion-based 3D concrete printing. Ma et al. Optimized magnesium phosphate cement formulations to achieve suitable properties for rapid-setting 3D printing applications [11]. Similarly, the incorporation of magnesium oxide into 3D-printed concrete has been studied to mitigate drying shrinkage and improve durability performance [12]. Other sustainable cementitious systems, such as limestone-calcined clay cement, have also been investigated as potential alternatives for reducing the environmental impact of construction materials. These materials exhibit promising characteristics for 3D concrete printing due to their mechanical performance and lower carbon footprint compared with conventional Portland cement systems [13]. In recent years, the use of waste-based materials in 3D concrete printing has become an important research direction within the framework of the circular economy. Several studies have investigated the incorporation of recycled materials and industrial by-products to reduce waste generation and improve the sustainability of printed structures. Skibicki et al. Investigated the reuse of fine recycled aggregates obtained from 3D-printed concrete and demonstrated that a closed-loop recycling approach could reduce cement consumption by 15%, although additional densification was required due to the porous structure of recycled aggregates [14]. Similarly, the incorporation of industrial by-products such as granulated blast furnace slag (GGBS) has been investigated as a partial replacement for cement in 3D concrete printing. Salleh et al. Demonstrated that a substitution rate of 40% GGBS could maintain a compressive strength of approximately 35 MPa while improving sustainability performance [15]. Butkutė et al. studied the use of carbonated slag granules in 3D concrete printing and reported a 20% improvement in thermal performance [16]. Other researchers have explored agricultural waste, recycled polymers, fibers, and various industrial residues as sustainable constituents for printable cementitious materials [17–19]. Among mining wastes, phosphate industry residues represent a significant resource due to their chemical composition and large availability, particularly in phosphate-producing countries such as Morocco. Waste rock, phosphogypsum (PG), and phosphate sludge generated during phosphate extraction and processing remain largely stored or landfilled, creating environmental challenges. However, their mineralogical composition, including calcium sulfate, calcium carbonate, and phosphate-containing phases, provides potential for their incorporation into cementitious materials [3,20]. Phosphogypsum has received particular attention as a secondary raw material for construction applications. Zhang et al. Reviewed phosphogypsum-based building materials and highlighted its potential for resource utilization while also identifying limitations related to impurities and processing requirements [20]. Furthermore, Sinka et al. Investigated the utilization of phosphogypsum through extrusion-based 3D printing and demonstrated its potential as a component of printable construction materials [21]. Recent studies have also explored phosphate mining by-products as alternative cementitious binders. Maliki et al. Investigated phosphate mine by-products for the production of eco-mortars and demonstrated their potential as new cementitious materials through experimental analysis and machine learning approaches [22]. These results confirm the possibility of transforming phosphate residues into valuable construction resources within a circular economy framework. The development of sustainable construction materials based on industrial waste is therefore an important research direction, particularly for countries with significant mining activities. The valorization of phosphate waste represents an opportunity to reduce environmental impacts associated with waste storage while providing alternative raw materials for the construction sector. In Morocco, the OCP Group has established ambitious strategies for the valorization of phosphate processing residues and the integration of circular economy principles into its industrial activities [3,22]. Mining operations, particularly open-pit mining, generate considerable quantities of waste rock. Waste rock corresponds to the non-economic fraction of extracted material that must be removed to access the valuable mineral deposit [4]. Compared with underground mining, open-pit mining generates higher volumes of waste materials, requiring appropriate management strategies to limit environmental impacts related to land occupation and contamination [23]. Consequently, the mining sector is increasingly focusing on circular economy approaches and the development of innovative solutions for waste reuse [24]. In this context, 3D concrete printing technology represents a promising pathway for the development of sustainable construction systems. By enabling automated fabrication,

reducing material consumption, and allowing the incorporation of alternative raw materials, 3D printing contributes to the evolution of Construction 4.0 and Construction 5.0 [25,26]. The integration of waste-derived materials into printable cementitious mixtures is particularly attractive because it combines the advantages of additive manufacturing with resource recovery strategies. Previous studies have demonstrated the feasibility of incorporating different industrial residues into 3D printable materials. Solid-waste-based cementitious materials have been reviewed as promising solutions for sustainable 3D concrete printing applications [8]. In addition, waste-based binders and recycled aggregates have shown potential for improving the environmental performance of printed structures [14,15]. However, the use of phosphate mining residues in 3D concrete printing remains insufficiently explored. Phosphate waste materials exhibit specific characteristics, including calcium-containing phases, suitable mineralogical compositions, and potential binding properties, making them promising candidates for additive manufacturing applications. Previous investigations have studied phosphate waste incorporation into cementitious systems, including the use of phosphate waste to improve fire resistance and modify cement properties [24]. Furthermore, phosphate-based materials such as phosphogypsum and phosphate residues have demonstrated potential for the production of alternative construction materials [20–22]. Therefore, the development of 3D-printable mixtures incorporating phosphate waste represents an innovative approach for combining industrial waste valorization, sustainable construction, and additive manufacturing technologies. In this study, three different waste materials generated from phosphate extraction and washing processes were investigated: waste rock, phosphogypsum (PG), and phosphate sludge. These materials, which are generally extracted and subsequently stored in disposal areas without significant added value, were characterized to evaluate their potential for construction applications. The objective of this work is to evaluate the physicochemical characteristics, thermal behavior, and potential applications of phosphate waste-based materials for sustainable construction using 3D concrete printing technology. The developed mixtures combine phosphate residues, red clay, crushed sand, and cement in order to obtain printable materials with suitable rheological and mechanical properties. The results obtained demonstrate the potential of phosphate waste valorization as a pathway toward the development of environmentally friendly construction materials and the promotion of circular economy principles.

2. Methods

Fifteen kilograms of phosphate waste from the Jadida phosphate processing plant were received. This waste was divided into three categories: waste rock, phosphogypsum, and sludge. It will be used for characterization and experimental analyses for the production of a construction material using 3D printing. Since some of this waste came from washing, moisture and mass tests were carried out. The waste was then oven-dried (figure 1,a, 1,b ,1,c), then ground (for the waste rock and sludge categories (figure 2,D, 2,E)), and finally sieved through a 250 μm screen (figure 2,F). This section presents various experimental characterization tests, including pH and moisture measurements.

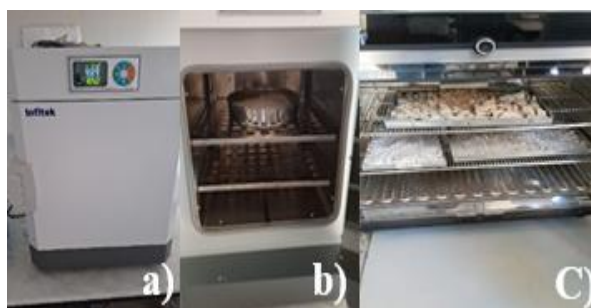


Fig 1. a) b) Oven at 105°C c) Phosphate waste in the oven



Fig 2. D) Sterile, E) Sludge, F) Sterile crushed

After crushing in a jaw crusher and disc mill, 8 kg of phosphogypsum were placed in an oven for 8 hours at a temperature of 105 °C and sterile and sludge were placed in the oven for 4 hours.

2.1 Moisture Content Test

Mass and moisture content were calculated using a moisture meter (figure 4, G, H). The moisture content before drying is indicated. The initial and post-drying masses had moisture contents ranging from 1.85% to 3.05% (*Table 1*) (*figure 3*). The analyzed phosphatation waste was extracted in May 2025 and transported from the OCP Jadida plant.

Table 1. Calculate the moisture content and mass before and after drying

Type of phosphate waste	Initial mass (g)	Mass after drying (g)	Humidity level before drying (%)
Steril	1894 g	1860 g	3.05%
Phosphogyps	240,6 g	194 g	15%
Phosphate sludge	1046 g	1036 g	1.85%

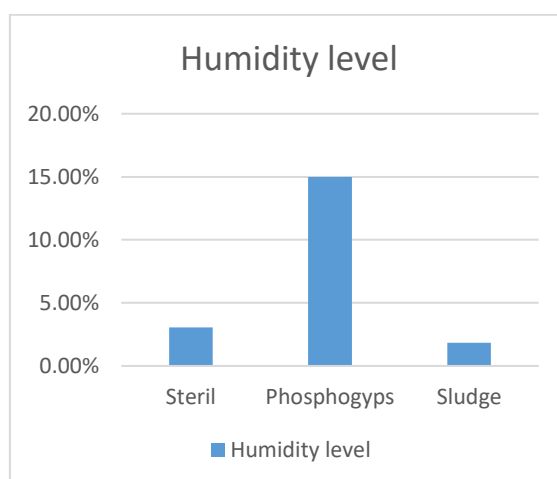


Fig 3. Calculate the moisture content and mass before and after drying



Fig 4. G) H) Moisture analyzer apparatus

For example, the second phosphogypsum sample extracted in July 2025: before drying, moisture content of 9% after drying, 10.48 g moisture content of 2.95% (*see table 2*).

Table 2. Moisture content before and after drying and measured mass for phosphogypsum

Type of phosphate waste	Humidity level before drying (%)	Mass (g)	Humidity level after drying (%)
Phosphogyps	9%	10,48 g	2,95%

2.2 pH Measurement Test

To determine the acidity or alkalinity of a liquid sample (phosphate slurry) 20 g of diluted material is taken in 101 g of sterile water after stirring for 20 min (figure 5, I), then the pH is calculated using a pH meter (figure 5, j) and the results were presented in Table 3.



Fig 5. i) Agitation apparatus (sludge diluted in sterilized water) j). pH meter measurement

Table 3. pH values measured for different types of phosphate waste using a pH meter

Type of phosphate waste	pH 1 (sample1)	pH 2 (sample2)	pH 3 (sample 3)
Steril	6,8	-	7,80
Phosphogyps	7,2	3,09	2,99
Phosphate Sludge	6,5	-	-

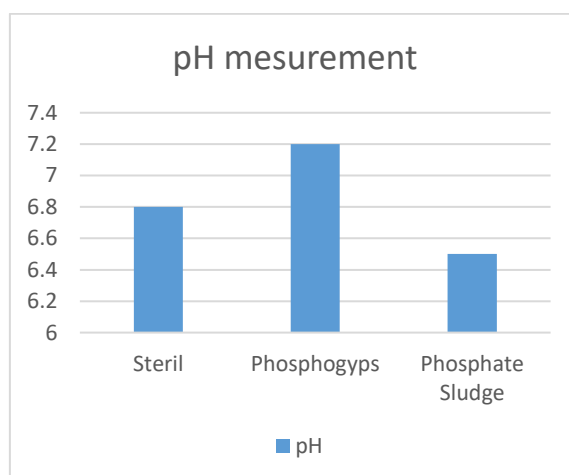


Fig 6. pH values measured for different types of phosphate waste using a pH meter

The three types of phosphate waste had pH values ranging from 6.5 to 7.8 (figure 6), indicating low acidity. The pH of two types of phosphate waste (sterile and phosphogypsum) was measured at different times. We found that the pH of phosphogypsum could vary between 2.99 and 7.2, while that of the sterile waste varied between 6.8 and 7.8.

2.3 Density Test

To determine the density (mass per unit volume) of a material, which is important for characterizing powders of waste phosphates (see table 4, figure 7).

Table 4. Density calculation

Type of phosphate waste	Density (g/cm ³)
Steril	2,7
Phosphogyps	2,55
Sludge	2,56

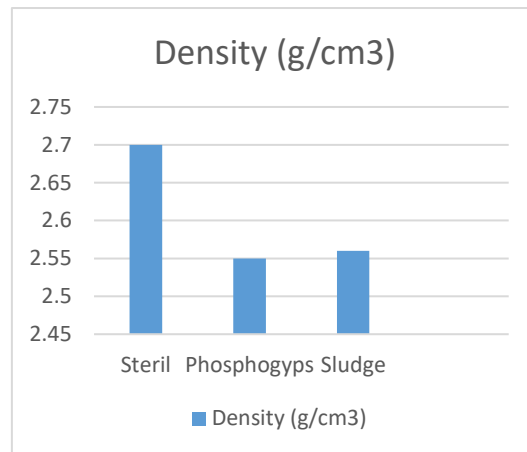


Fig 7. Density calculation

The density varies slightly, from 2.5 to 2.7 g/cm³, depending on the type of phosphate waste; this is a very low density.

2.4 VPS (Volume Percent Solids) Calculation

VPS is often used in suspensions, slurries or inks to determine the percentage of solid particles by volume in a mixture (see Table 5, figure 8).

A pycnometer determines density by measuring the mass of a known volume (figure 9). For powders: the pycnometer is filled with a liquid (usually water) and powder, and the displacement of the liquid gives the volume of powder.



Fig 8. Pycnometer method

Table 5. VPS (Volume Percent Solids) Calculation

Components	Volume fraction (VPS, %)
Crushed sand 250	0.09
Crushed sand 160	0.10
Red Clay	10,81
Steril	2,15
Sludge	1,19

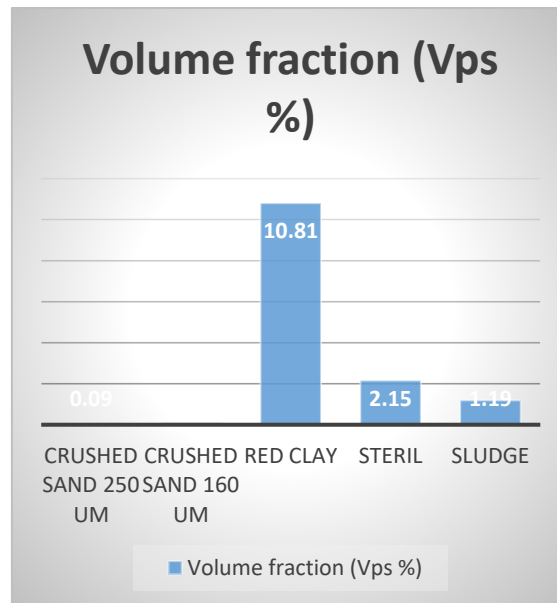


Fig 9. VPS (Volume Percent Solids) Calculation

The volume fraction (Vps) was calculated for the different components, such as crushed sand of less than 250 μm , its Vps value is 0.09%, and for crushed sand of less than 160 μm , the Vps value is 10.81%, red clay is about 2.15%, rock waste is about 1.19% and sludge is about 0.09%.

2.5 Leaching Test

2.5.1 Leaching Test

The leaching test is used to evaluate the release of soluble substances from a solid material when it comes into contact with a liquid, usually water or a specific extraction solution. This is important for assessing environmental impact, chemical stability, and material safety (see table 6).

Table 6. Leaching Test

Sample reference	A preliminary pH test	pH of the leachate	Weight loss (%)
Phosphogyps	2,05	4,94	14,02
Steril	4,48	7,16	5,53

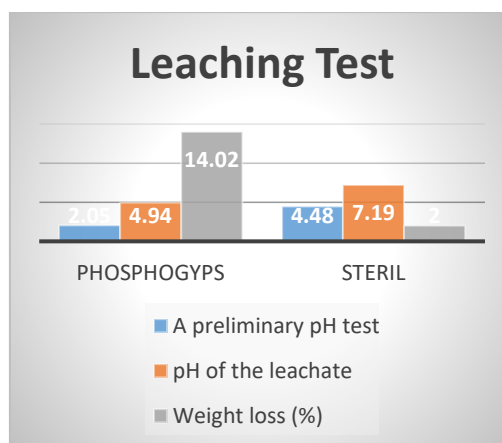


Fig 10. Leaching Test

During the leaching test (see table 6), (figure 10), the pH of phosphogypsum was calculated at 2.05, and the pH of the leachate was 4.94, the weight loss was approximately 14.02%, and for the sterile control, the pH was 4.48, the pH of the leachate was approximately 7.16 and the weight loss was 5.53%.

2.5.2 Method: TCLP (Toxicity Characteristic Leaching Procedure)

ICP-OES (Inductively Coupled Plasma – Optical Emission Spectroscopy) with reference *ICP-OES PerkinElmer Avio 550 Max* is used to **quantify elemental composition** in liquid samples (figure 11) , such as leachates from TCLP or digested powders. It allows detection of **metals and some non-metals** with high sensitivity and accuracy.

The TCLP method (EPA 1311) assesses the mobility of inorganic species in a residue to determine whether it is considered leachable according to regulations (see *Table 7*). It is based on leaching with an acetic acid solution under controlled conditions of time and agitation.



Fig 11. Samples containing an acetic acid solution

Table 7. ICP-OES (Inductively Coupled Plasma – Optical Emission Spectroscopy)

Sample Id	Ag (ppm)	As (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (ppm)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Nb (ppm)	Li (ppm)
Phosphogyps	0,37	0,30	0,40	0,29	<0,1	1036,71	0,46	0,28	0,25	0,29	0,34	<0.1	0,13
	Fe (ppm)	K (ppm)	Mg (ppm)	Mn (ppm)	Na (ppm)	Ni (ppm)	Pb (ppm)	Sr (ppm)	V (ppm)	Zn (ppm)	Mo (ppm)	Sb (ppm)	
	0,50	4,23	8,32	0,25	1516,61	0,23	0,25	8,17	0,32	2,24	<0.1	<0.1	
Steril	Ag (ppm)	As (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (ppm)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Nb (ppm)	Li (ppm)
	0,36	0,30	0,48	0,29	<0,1	622,89	0,26	0,28	0,25	0,27	0,28	<0.1	0,11
	Fe (ppm)	K (ppm)	Mg (ppm)	Mn (ppm)	Na (ppm)	Ni (ppm)	Pb (ppm)	Sr (ppm)	V (ppm)	Zn (ppm)	Mo (ppm)	Sb (ppm)	
	0,44	11,10	113,11	0,27	1357,63	0,25	0,23	1,44	0,33	0,32	<0.1	<0.1	

The ICP-OES test shows that sterile gypsum and phosphogypsum do not contain heavy metals and that all hazardous chemical elements are negligible.

2.6. Loss on Ignition (LOI) Test

The Loss on Ignition (LOI) test of phosphate waste determines the volatile fraction of the material, including moisture, organic matter, and carbonate content. This analysis is important because: Phosphate waste contains organic residues, adsorbed water, and carbonates. Heating the sample to a high temperature causes these components to decompose or evaporate, and the mass loss is expressed as a percentage of the initial mass.

This test determines the volatile fraction (moisture, organic matter, carbonates) of phosphate waste. It also allows for: Heating phosphate waste to a high temperature eliminates the volatile components, and the mass loss is measured as a percentage of the initial mass.

With the loss on ignition test, the organic matter and bound water in the sample are measured; 20 g was measured and prepared in a muffle furnace (heated to 950 °C for 3 hours (*figure 12*)), weighed before and after heating, and then the mass loss was calculated.



Figure 12. Glass filled in a muffle furnace (heated to 950C° for 3 hours)

Table 8. Loss on ignition and sterile fraction of phosphate waste

Type of phosphates waste	Radioactive activity (Bq/cm²) Radioactivity in general of Alpha, Beta And Gamma:
Sterile	0.271
Phosphogyps	0.603
Sludge	0.904

Glass filled with waste of phosphate in a muffle oven (heated to 950C° for 3 hours) Mass loss allows us to determine the mass percentage of CO₂ contained in the ore.

Previously dry crucibles, filled with an arbitrary mass of the sample, are heated in a furnace at 950°C for two hours with an optional preheating rate (*Figure 12*). The difference in mass before and after the heating process is used to calculate the loss on ignition.

The formula for calculating mass loss is: $LOI = (M_i - M_f) / M_i \times 100$ with: law (lost on ignition)

With M_f is the final mass of the sample and M_i is the initial mass of the sample.

The percentage of mass loss of phosphate sludge is 17.30% and that of phosphogypsum is 16.51% and 17.67% of sterile (*see table 8*).

2.7 Radioactive Activity Measurement – Apparatus

To measure the **radioactivity** (decay rate) of a radioactive sample (*figure 13*), expressed in **Becquerels (Bq)** or **Curies (Ci)**. This is important for Radioactive materials emit **ionizing radiation** (α , β , or γ rays).

Table 9. Radioactive activity (Bq/cm²) Radioactivity in general of alpha, beta and gamma radiation for each type of phosphate waste

Type of phosphates waste	Empty tare (g)	Test portion (Mass calculation) (g)	Masse calculation (Mf)	Full tare (g)	% Mass Loss
Phosphate Sludge	34,9492	20,7789	17,1836	52,1328	17,30%
Phosphogyps	35,9176	17,7749	14,8394	50,7570	16,51%
Sterile	34,9527	16,6819	13,733	48,6857	17,67 %



Fig 13. Radioactive Activity Measurement – Apparatus

Phosphate ores often contain uranium and thorium traces, which are naturally radioactive. Measuring radioactive activity ensures environmental safety and compliance with regulations. Helps evaluate potential

radiological risk when using phosphate waste for construction. The radioactivity of the three types of phosphate waste shows a low radioactivity which varies between 0.271 (Bq/cm²) and 0.904 Bq/cm² (see table 9).

3. Mineralogical And Chemical Composition

Chemical analysis of the powder samples was performed by X-ray fluorescence spectroscopy using a Malvern Panalytical "Epsilon 4" energy-dispersive spectrometer. Approximately 1 g of each sample was measured:

3.1 X-ray fluorescence spectroscopy (XRF) Test

XRF is used to determine the elemental composition of solid or powdered samples with reference *Pan Analytical, Epsilon 4*. For phosphate waste, it helps to identify and quantify : Major elements: Ca, P, Si, Fe, Al, Mg Trace elements or contaminants: Pb, Cd, As, Cr Evaluate the material's suitability for 3D printing, reuse, or environmental safety. To determine the XRF spectrum of each component, the density of each material must be known; the densities found in the previous section were used.

a) XRF Sludge sample

XRF analysis shows that the sludge is composed of 13,835% of SiO₂ , and 31,203% et 2,087% of SO₃ , 1,2087% of Cl , 0,432% of K₂O, 49,876% of CaO , 0,281% of TiO₂ , 0,743% Fe₂O₃, that the other components are negligible, such as NiO , CuO , ZnO , SrO , Y₂O₃, ZrO₂, SnO₂, Eu₂O₃, Yb₂O₃, Re, U (see table 10).

Table 10. Chemical analysis by the XRF method of sludge

Compound	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O
Conc Unit	13.835%	31,20 3%	2.08 7%	1.29 8%	0.432 %
	SrO	Y ₂ O ₃	ZrO 2	SnO 2	U
	161,9 ppm	43,7p pm	13,7 ppm	32,3 ppm	33.7 ppm
	CaO	TiO ₂	V ₂ O 5	Cr ₂ O ₃	MnO
	49,876%	0 ,281 %	952. 2 ppm	702. 1 ppm	62,7 ppm
	Fe ₂ O ₃	NiO	ZnO	CuO	
	0.743%	124.5 ppm	233. 0 ppm	79,2 ppm	

b) XRF Steril sample

XRF analysis shows that the Steril is composed of 1,380% of MgO, and 2,859% of Al₂O₃, 13,007% of SiO₂, 16,463% of P₂O₅, 0.713% SO₃, 0.144% Cl , 0.597% K₂O , 60,827% CaO , 0.404% TiO₂, 3,012% Fe₂O₃, 0,101% ZnO , 0,132% that the other components are negligible, such as V₂O₅, MnO , NiO , CuO , Ga₂O₃, As₂O₃, SeO₂, Br, Rb₂O, Y₂O₃, ZrO₂, Nb₂O₅, CdO, SnO₂, Sb₂O₃, TeO₂, BaO, Sm₂O₃, Lu₂O₃, IrO₂ (see table 11).

Table 11. Chemical analysis by XRF method of Steril

Compound	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl
ConC Unit	1,380%	2,859%	13,007%	16,463%	0.713%	0,144%
	MnO	Fe₂O₃	NiO	CuO	ZnO	Ga₂O₃
	26,0 ppm	3,012%	337,0 ppm	101,1 ppm	0.101%	11,9 ppm
	Y₂O₃	ZrO₂	CdO	SnO₂	Sb₂O₃	TeO₂
	278,8 ppm	176,4 ppm	83,3 ppm	100,6 ppm	43,6 ppm	91,5 ppm
	K₂O	CaO	Br	Cr₂O₃		
	0.597%	60,827%	2,6 ppm	0.108%		
	As₂O₃	SeO₂	V₂O₅	SrO		
	43,2 ppm	3,5 ppm	848.5ppm	0,132%		
	BaO	TiO₂	Rb₂O			
	152,9 ppm	0.404%	25,3 ppm			

C) XRF phosphogyps sample

XRF analysis shows that the phosphogyps is composed of 1,290% MgO, 1,262% SiO₂, 1,700% P₂O₅, 49,677% SO₃, 45,861% CaO, and that the other components are negligible, such as Cl, Ti, V, Cr, Fe₂O₃, Zn, As, Se, Sr, Y, Zr, Nb, Sn, Sb, Te, Ba, Ce, Nd, Sm, Pb, U, Gd, Yb, Lu, Re (see table 12).

Table 12. Chemical analysis by XRF method of Phosphogyps

Compound	MgO	SiO ₂	P ₂ O ₅	SO ₃	CaO	Ti
Conc unit	1,290 %	1,262 %	1,700 %	49,6 77%	45,861 %	233, 1 ppm
	Se	Sr	Y	Zr	Nb	Sn
	1,7 ppm	847,5 ppm	172,4 ppm	15,8 ppm	0.3 ppm	51,4 ppm
	V	Cr	Fe₂O₃	Zn	As	Yb
	10,9ppm	23,2ppm	478,3ppm	5,0ppm	1,7ppm	29,8 ppm
	Sb	Te	Ba	Ce	Pb	U
	25,4 ppm	53,0 ppm	93,3 ppm	42,1 ppm	2,1 ppm	16,6 ppm

3.2 XRD Test (X-ray Diffraction Analysis)

X-rays hit a crystalline sample, they are diffracted in specific directions depending on the atomic arrangement. By measuring these diffraction patterns, we can determine what phases are present.

Here, Phase identification of the phosphate waste-based materials was carried out using X-ray diffraction (XRD) analysis with reference *bruker, discover d8* (see figure 14, 15, 16).

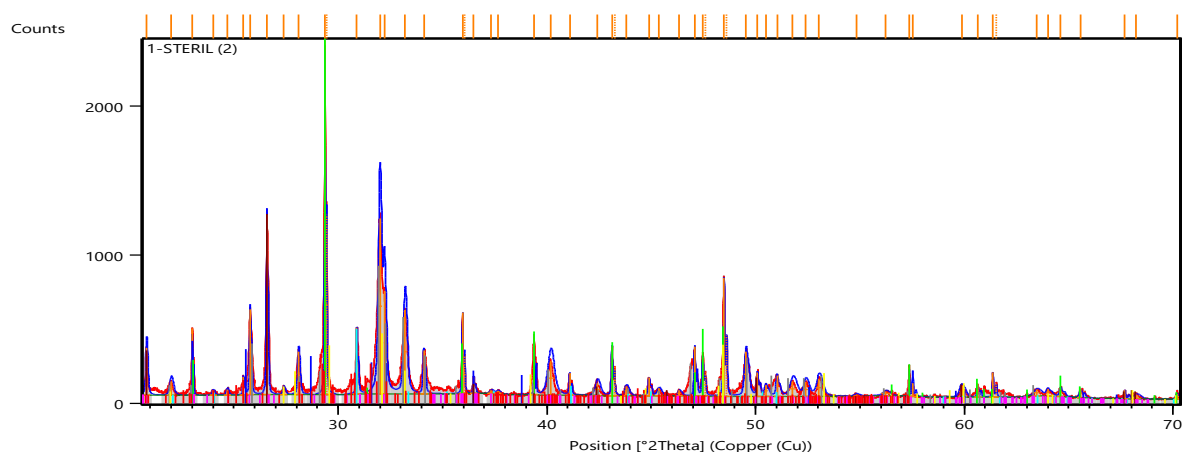


Fig 14. X-ray Diffraction pattern of the steril sample

In the figure 14, using high-performance software, peaks were found in the XRD results curve of steril sample.

Accepted Ref. Pattern: 96-900-5250							
No.	Visi...	Ref. Code	Compound Name	Chemical Formula	Score	SemiQuant [%]	Display Color
1	☒	ICDD 00-003-0163	Calcium Sulfate	Ca S O ₄	24	-	Blue
2	☒	ICDD 01-072-1937	Calcium Carbonate	Ca C O ₃	55	-	Lime
3	☒	ICDD 00-015-0876	Calcium Fluoride Phosph...	Ca ₅ (P O ₄) ₃ F	43	-	Gray
4	☒	ICDD 01-089-1961	Silicon Oxide	Si O ₂	42	-	Maroon
5	☒	ICDD 96-900-3522	Dolomite	Ca _{3.00} Mg _{3.00} C...	34	-	Aqua
6	☒	ICDD 96-900-2780	Montmorillonite	Al _{4.00} Si _{8.00} O _{2...}	17	-	Fuchsia
7	☒	ICDD 01-075-2235	Copper Sulfide	Cu S	20	-	Yellow
8	☒	ICDD 96-900-5250	Altisite	K _{11.00} Na _{7.00} Ti...	16	-	Red

Figure 15. The chemical components of the sterile sample, X-ray diffraction results displayed in the Highscore software

Using High Score software, we observe that the peaks of the XRD result curve of Steril, the chemical characterization of Steril represents calcium sulfate, calcium carbonate, calcium fluoride, phosphogypsum, silicon oxide, dolomite, montmorillonite, copper sulfide and altisite (*figure 15*).

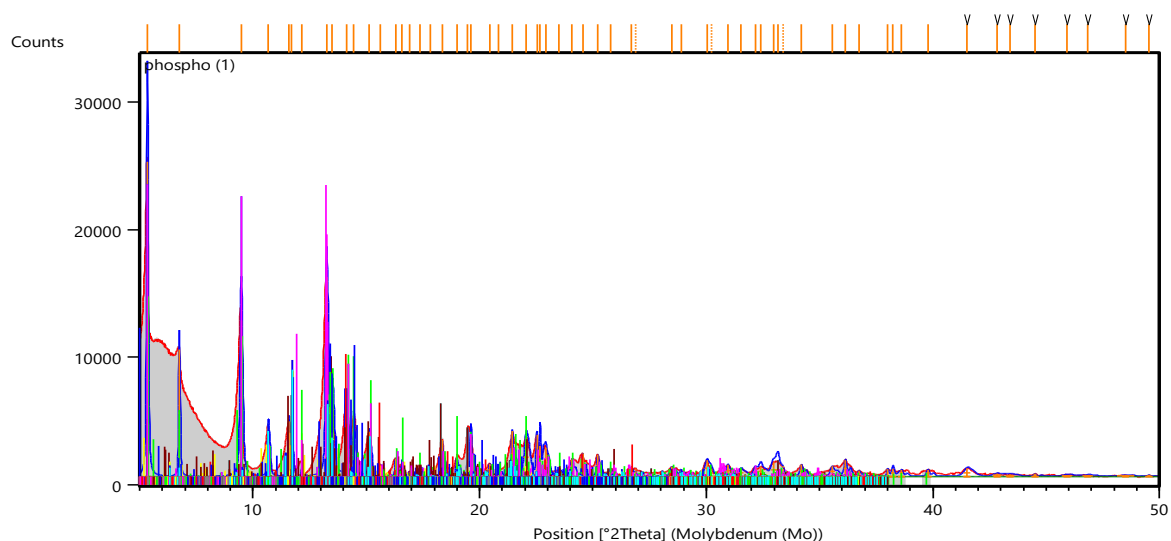


Fig 16. X-ray Diffraction pattern of the Phosphogypsum sample

In the figure 16, using high-performance software, peaks were found in the XRD results curve of phosphogypsum.

No.	Visi...	Ref. Code	Compound Name	Chemical Formula	Score	SemiQuant [%]	Display Color
1	☒	00-035-0614	Cerium Phosphate Hydrate	$\text{Ce P O}_4 \cdot \text{H}_2 \text{O}$	53	-	Lime
2	☒	96-900-5482	Heulandite-Ca	$\text{Na}_{1.72} \text{Ca}_{0.40} \text{C}...$	34	-	Maroon
3	☒	96-900-4440	Marialite	$\text{Na}_{6.88} \text{K}_{0.56} \text{Ca}...$	37	-	Aqua
4	☒	96-900-4441	Marialite	$\text{Na}_{7.04} \text{K}_{0.32} \text{Ca}...$	37	-	Yellow
5	☒	96-900-4439	Marialite	$\text{Na}_{7.04} \text{K}_{0.56} \text{Ca}...$	37	-	Blue
6	☒	01-089-7418	Sodium Calcium Aluminu...	$(\text{Na}_{2.62} \text{Ca}_{1.33})...$	35	-	Gray
7	☒	96-900-0369	Eucryptite	$\text{Si}_{12.00} \text{Al}_{12.00} \text{L}...$	34	-	Maroon
8	☒	96-900-9519	Plumbonacrite	$\text{Pb}_{30.00} \text{C}_{18.00} ...$	35	-	Aqua
9	☒	00-042-1389	Thorium Phosphate Hydr...	$\text{Th P O}_4 \cdot \text{H}_2 \text{O}$	43	-	Fuchsia
10	☒	96-901-0786	Effenbergerite	$\text{Ba}_{2.00} \text{Sr}_{2.00} \text{Cu}...$	33	-	Yellow
11	☒	96-900-3052	Kosmochlor	$\text{Na}_{4.00} \text{Cr}_{4.00} \text{Si}...$	31	-	Red

Fig 17. The chemical components of the Phosphogypsum sample, X-ray diffraction results displayed in the Highscore software

Using High Score software, we observe that the peaks of the XRD result curve of Phosphogypsum the chemical characterization of Phosphogypsum represents Cerium Phosphate hydrate , heulandite-Ca , Marialite , Sodium Calcium Aluminium , Eucryptite , plumbonacrite, thorium phosphate , effenbergerite , kasmochlor (figure 17).

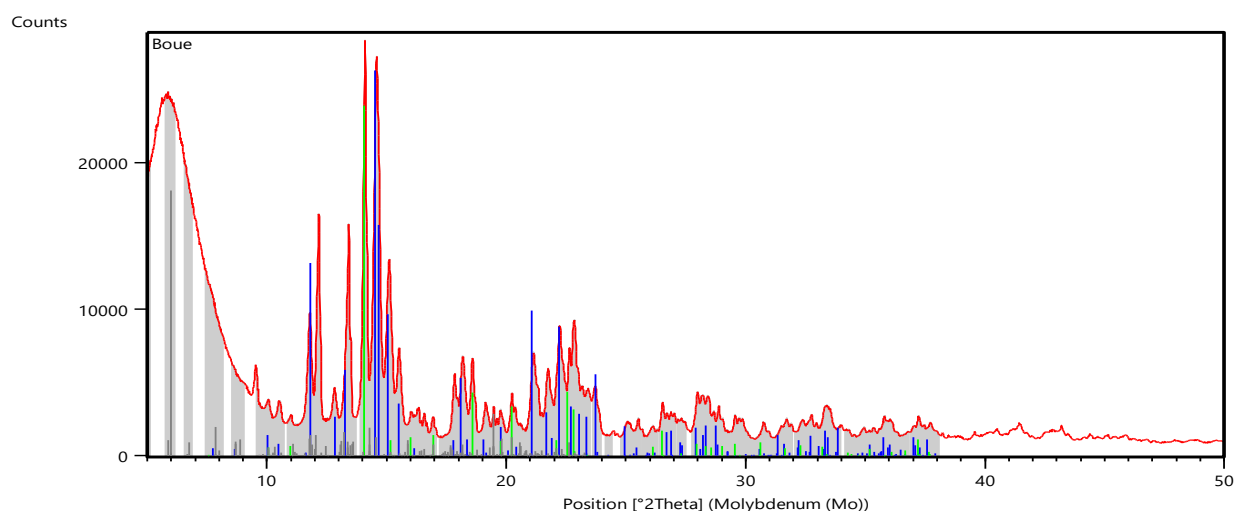


Fig 18. XFig. 1. X-ray Diffraction pattern of the Sludge sample

In the figure 18, using high-performance software, peaks were found in the XRD results curve of Sludge Sample.

No.	Visi...	Ref. Code	Compound Name	Chemical Formula	Score	SemiQuant [%]	Display Color
1	☒	96-900-1345	Fluorapatite	$\text{Ca}_{9.28} \text{Na}_{0.10} \text{C}...$	82	48	Blue
2	☒	96-900-0084	Dolomite	$\text{Ca}_{3.00} \text{Mg}_{3.00} \text{C}...$	76	19	Lime
3	☒	96-900-5691	Nobleite	$\text{Ca}_{4.00} \text{B}_{24.00} \text{O}...$	55	33	Gray

Fig 19. The chemical components of the sludge, X-ray diffraction results displayed in the Highscore software

Thanks to powerful analysis software, we observe that the peaks of the X-ray diffraction curve of the mud, whose chemical characterization corresponds to fluorapatite, dolomite and nobleite, are present (figure 19).

4. Investigation of eco-materials from phosphate waste for 3D concrete printing

Following the characterization and experimental investigation of eco-materials from phosphate waste for 3D concrete printing, in this part, we will present a methodology for preparing mixed phosphate waste, such as mixing and the step-by-step procedure, in accordance with standards, with the following tests: crush and tensile breakage tests of samples of different mixtures, shear and triaxial tests, viscosity and consistency tests, and finally rheology tests and morphological analysis (SEM).

4.1 Formulations: Mixing procedure and step-by-step instructions according to standards

The preparation of cementitious material samples is carried out in accordance with applicable standards (such as EN 196-1 or ASTM C109) to ensure the reproducibility and reliability of experimental results. The process begins with the precise dosing of raw materials (Figure 20 a, b, c),

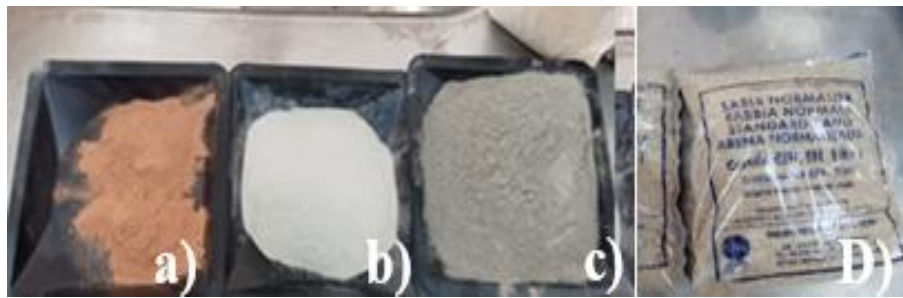


Fig 20. a) Red clay, b) Crashed sand, c) Cement, d) Standardized sand

including cement (In our study, three cement types (C25, C45, and C65) were tested, using approximately 265 g of cement and 100 g of phosphate waste per formulation), phosphate waste (waste rock, phosphogypsum, sludge), red clay (30 g if necessary), standardized sand (Figure 20 d), and sterile water. Different water dosages, ranging from 145 g to 185 g, were also tested depending on the mixture consistency and the results of the Vicat test. The optimal water dosage was found to range from 145 g to 170 g. The proportions were determined according to the formulation under investigation (see Table 13).

Table 13. Formulation of phosphate waste mixture (for one test tube 4×4×16 cm³)

Component	Mass (g)	Comment
CEM I 52.5	265 g	High dosage for performance
Crashed Sand under 250 µm	150 g	Main aggregate
Phosphate waste (Steril or sludge or gypsum)	100 g	Well ground and homogeneous
Red clay	30 g	Improves cohesion
Water (W/C ~ 0.38)	145 g	Calculated for resistance

The mixing is carried out using a standard mortar mixer (Figure 21e). The dry components are first introduced into the mixing bowl and mixed at low speed for a predetermined time to ensure initial homogenization. Water is then added gradually, and the mixing continues according to a sequence of speeds and times prescribed by the standard, until a homogeneous paste or mortar, free of lumps and with a uniform consistency, is obtained. After mixing, the fresh material is poured into a standardized mold. Cubic molds measuring 4 x 4 x 16 cm³ (Figures 21e and 21f), previously cleaned and lightly oiled to facilitate demolding, are used. The molds are filled in one or more layers, each layer being compacted by mechanical vibration using a mixer (Figure 21, G) to eliminate air bubbles and ensure optimal compaction. The test specimens are then surface-smoothed (Figure 21, H) and kept in their molds at room temperature, protected from evaporation, for the first 24 hours (Figure 21, I).



Fig 21. E) Mortar mixer, F) Mold samples 4×4×16 cm³ G) Vibrating table to eliminate air H) Mold filled with mixture I) pockets in samples Cover in a damp room, J) The samples in the water.

After demolding, the samples are stored in water (Figure 21, J) in a humidity-controlled chamber (temperature $\approx 20\text{ }^{\circ}\text{C}$, relative humidity $\geq 95\%$) until the expected test age (7, 14, or 28 days). This step is essential to ensure the proper development of the cementitious material's mechanical and microstructural properties. Three standardized reference mixtures, composed of different types of cement (C25, C45, and C65) (see *table 14*), were prepared, as well as 17 different mixtures of phosphate waste (see *table 15*, *16*, *17*).

Table 14. Basic formula of reference types of C25, C45 and C65 cements (for a 4×4×16 cm³ sample)

Referenc es	Type of cement	Cement (g)	Standardiz ed sand (g)	Sterilized water (g)
R1-25	C25	150 g	450 g	75 g
R1-45	C45	150g	450 g	75 g
R1-65	C65	150g	450 g	75 g

Table 15. Mix proportions of formulations M1–M5 prepared with C25 cement

Blend	Cement C25 (g)	Red Clay (g)	Sand (g)	Sand type	Sterile (g)	Phosphogyps (g)	Sludge (g)	Sterilized water (g)
M1-25	265	30	150	Crushed sand	40	40	20	145
M2-25	150	30	450	Crushed sand	30	40	30	145
M3-25	265	30	150	Crushed sand	50g	50g	0g	145
M4-25	265	30	150	Crushed sand	44.5g	11g	44.5g	145
M5-25	265	30	150	Crushed sand	100	0	0	145

Table 16. Mix proportions of formulations M1–M8 prepared with C45 cement

Blend	Cement C45 (g)	Red Clay (g)	Sand (g)	Sand type	Sterile (g)	Phospho gyps (g)	Sludge (g)	Sterilized water (g)
M1-45	265	30	150	Crushed sand 250 Um	100	0	0	145
M2-45 (F6)	265	30	150	Crushed sand	42,5	15,45	42,5	170
M3-45 (F3)	265	30	150	Crushed sand	25	50	25	145
M4-45 (F4)	265	30	150	Crushed sand	50	25	25	145
M5-45 (FBS)	265	30	150	Crushed sand	50	0	50	145
M6-45	265	30	150	Standardized Sand	100	0	0	145
M7-45 (145g)	265	30	150	Crushed sand	100	0	0	145
M8-45 (170g)	265	30	150	Crushed sand	100	0	0	170

Table 17. Mix proportions of formulations M1–M4 prepared with C65 cement.

Blend	Cement C65(g)	Red Clay (g)	Sand (g)	Sand type	Sterile (g)	Phosphogyps (g)	Sludge (g)	Sterilized water (g)
M1-65	265	30	150	Crushed sand	100	0	0	177
M2-65	265	30	150	Crushed sand	100	0	0	160
M3-65	265	30	150	Crushed sand	100	0	0	185
M4-65	265	30	150	Crushed sand	100	0	0	170

The appropriate formulations were identified within the E/L range of 0.5 – 0.6.

4.2 Crushing and Tensile Breakage Testing of Specimens of Different Mixtures

Crushing, bending, and compression failure tests were performed on the reference samples (Figure 22, K, L) and on the different mixtures (see, for example, Figure 23, M, N). More than 17 mixing and crushing cycles, involving over 50 samples (Each specimen was prepared in triplicate). Were carried out to compare and evaluate the mechanical behavior of the prepared samples under compressive and bending loads. These tests provide insight into the material's strength, failure modes, and overall durability—all essential elements for assessing its suitability for construction and 3D printing applications.

All samples were subjected to controlled loading conditions until failure, at a rate of 0.500 MPa/s and an initial force of 0.500 kN, with a stopping force of 10%. The maximum load and failure mode were recorded for analysis in Tables 31, 32, and 33.



Fig 22. Samples of the references



Fig 23. Samples of mixture M1/M6

Before the test, our sample was weighed. After 28 days, its weight was approximately 526.58 g (Figure 24).



Fig 24. Weight Of Specimen

5. Result

5.1 Compressive and flexural strength

This section presents grouped bar charts comparing the compressive and flexural strengths of mixtures prepared with C25, C45, and C65 cement.

This work presents the results obtained on 23 ground samples of our mixture with cement 25 (M-25) and 6 reference samples (R-25). The tables show the flexural and compressive strength results as a function of dimensional stress and strength. This test was performed using the Controlab compression machine, reference C57F02/M (Figure 25).



Figure 25. Compression Measuring Machine

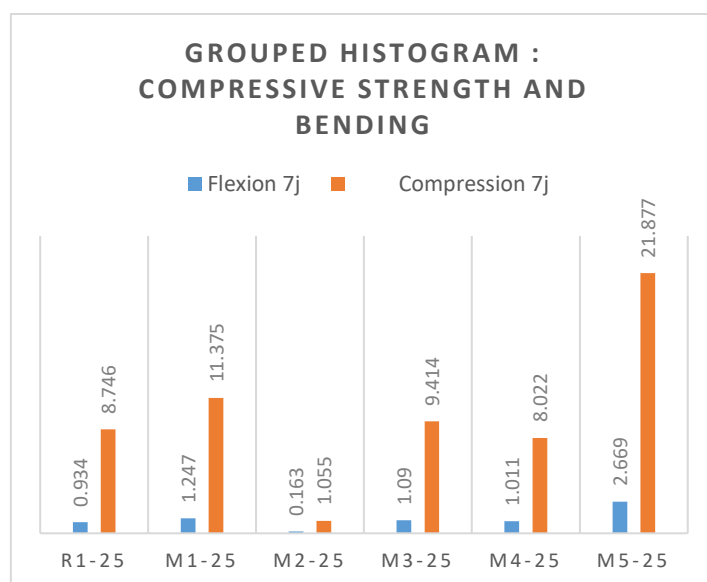


Fig 26. Grouped bar chart of the 7-day compressive and flexural strengths of mixtures prepared with C25 cement.

Figure 26 presents a clustered bar chart comparing the compressive and flexural strengths of the five mixtures prepared with C25 cement (M1-C25 to M5-C25) with those of the reference material (R1-C25). The results show that mixtures M1-C25, M3-C25, and M5-C25 exhibit higher compressive strengths after 7 days of curing than the reference mixture. Among the tested formulations, M5-C25 achieves the highest compressive strength, reaching 21.877 MPa, compared with 8.746 MPa for the reference mixture R1-C25. These findings highlight the potential of incorporating phosphate-industry by-products into cementitious mixtures, although further testing is required to establish their suitability for 3D concrete printing applications.

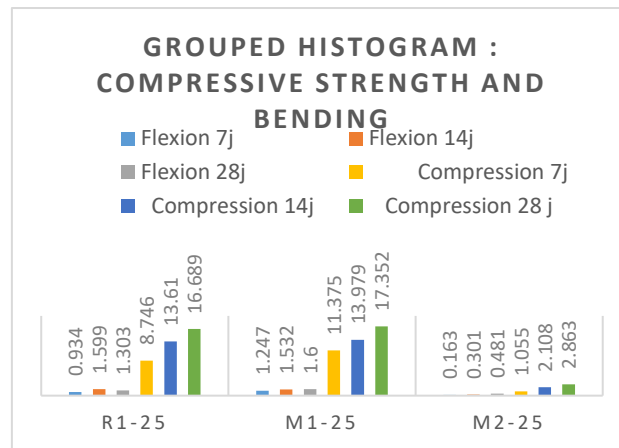


Fig 27. Grouped bar chart of the compressive and flexural strengths of mixtures prepared with C25 cement after 7 and 14 days of curing, and their compressive strength after 28 days.

As shown in Figure 27, the clustered histogram compares the compressive and flexural strengths of C25 concrete mixtures M1 and M2 with the reference material R1-25 at 7, 14, and 28 days, highlighting the influence of curing on the development of mechanical properties

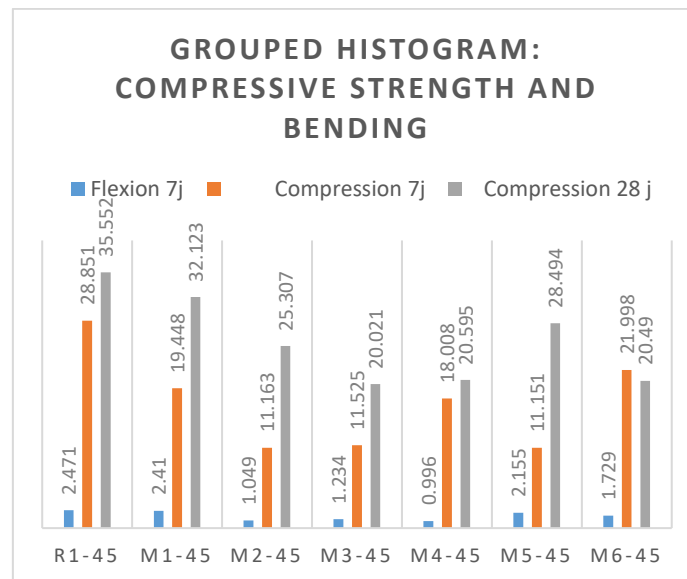


Fig 28. Grouped bar chart of the compressive and flexural strengths of mixtures prepared with C45 cement after 7 days of curing, and their compressive strength after 28 days of curing.

In this study, the results obtained from 31 ground specimens of the mixtures prepared with C45 cement (M-45) are presented and compared with those of four reference specimens (R-45). The tables report the flexural and compressive strength results, calculated based on the measured dimensions and the corresponding failure loads.

Figure 28 and 29 shows the grouped histogram of compressive and flexural strength with C45 cement, as well as the comparison of the eight mixtures of our materials with the standardized reference. Mixtures M1 and M7 exhibited high compressive strengths after 28 days of curing, with values comparable to that of the R1-45 reference mixture. This result highlights the potential of the developed materials. Mixture M1 achieved the highest compressive strength among the investigated mixtures, reaching 32.123 MPa, compared with an average compressive strength of 32.60 MPa for the R1-45 reference mixture, calculated from six specimens.

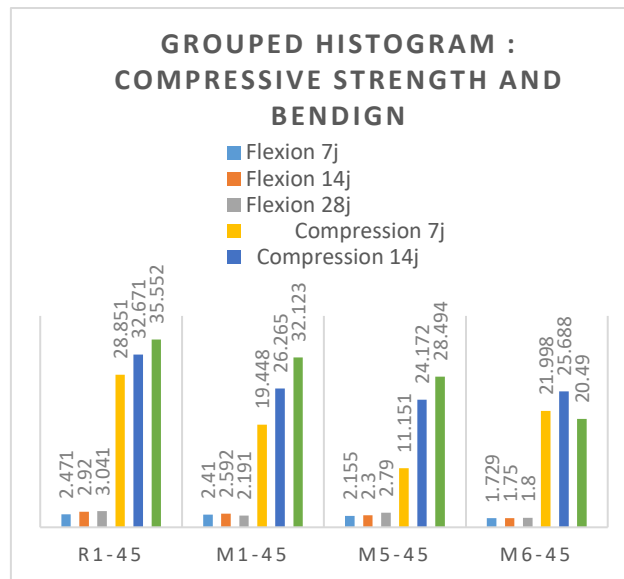


Fig 29. Grouped bar chart of the compressive and flexural strengths of of mixtures prepared with C45 concrete after 7, 14 and 28 days of curing.

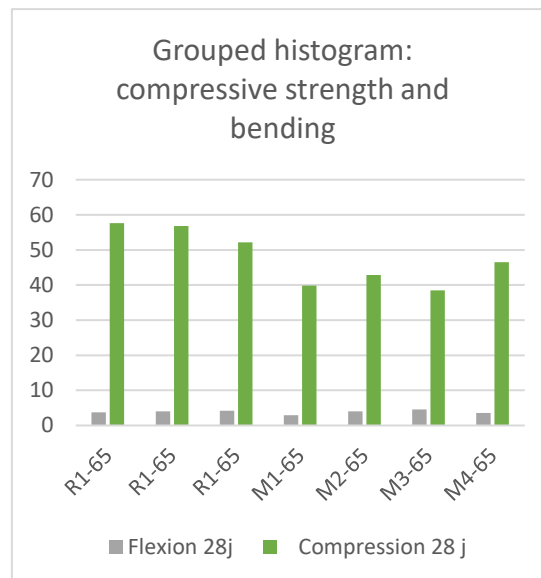


Fig. 30. Grouped bar chart of the compressive and flexural strengths of mixtures prepared with C65 concrete after 28 days of curing.

This project presents the results of seventeen samples of our mixture with C65 cement (M-65), with six reference samples R- 65. The table below shows the flexural and compressive strength results as a function of dimensional stress and strength.

Figure 30 shows the grouped histogram of compressive and flexural strength with C65 cement, as well as the comparison of the four mixtures of our materials with the standardized references. Mixture M4 exhibited the highest compressive strength among the investigated mixtures after 28 days of curing. Although its strength did not exceed that of the R1-65 reference mixture, the value obtained was relatively close, highlighting the potential of the developed materials. The highest compressive strength was recorded for M4-65, reaching 46.528 MPa, compared with an average compressive strength of 54.56 MPa for the R1-65 reference mixture, calculated from eight specimens.

5.2 Shear test

The shear test is used to evaluate the shear strength and mechanical behavior of cementitious materials subjected to shear stresses, using a MATEST A129 reference shear testing machine (SN: A129/BD/0008). It allows for the analysis of the material's ability to resist slippage and failure under shear forces, an essential condition for structural applications. The sample, with a standardized geometry with the following dimensions $13,7\text{ cm} \times 6,4\text{ cm}$ (Figure 31), is placed in a direct shear device where a load is applied parallel to the predefined shear plane. The load is increased gradually and in a controlled manner until the sample fails. During the test, the pressure is recorded as a function of time (Figure 32). It reaches 0.30 MPa at 150 seconds, then stabilizes linearly until 560 seconds, before decreasing to 0.23 MPa.



Fig 31. Mold and test specimen for shear testing

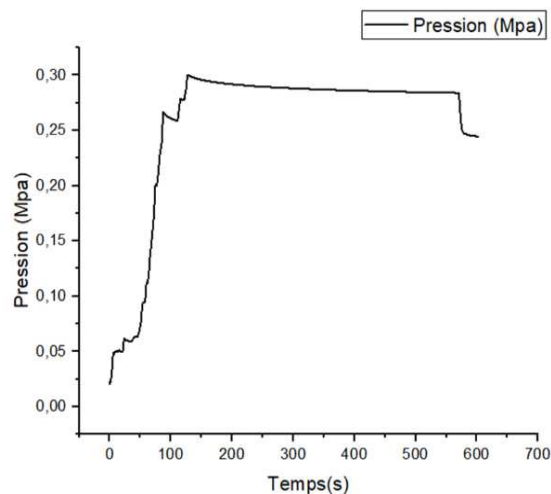


Fig 32. Pressure (MPa) as a function of time (s) – shear test result

5.3 Triaxial test

The triaxial test characterizes the mechanical behavior of a material subjected to multiaxial loading by reproducing confinement conditions close to those encountered in situ, using a MATEST A142N reference triaxial machine (serial number: BB/0002). It allows for the analysis of the material's strength, deformability, and failure mechanisms. The Specimen mold for triaxial compressive strength testing, with the following dimensions $10,5\text{ cm} \times 3,40\text{ cm} \times 13,7\text{ cm}$. (See Figure 33) is placed in a triaxial cell and subjected to a uniform confining pressure applied radially by compressed air. An increasing axial load is then applied in a controlled manner until failure or until a predefined deformation level is reached, with the Confining pressure maintained constant (see table 18).

Table 18. Calculation of triaxial test resistance

	Duration of time	Resistance	Maximum load	Test speed
Shear modulus (triaxial)	7 jr	12,224 MPa	39.32 kN	0.086 MPa/s

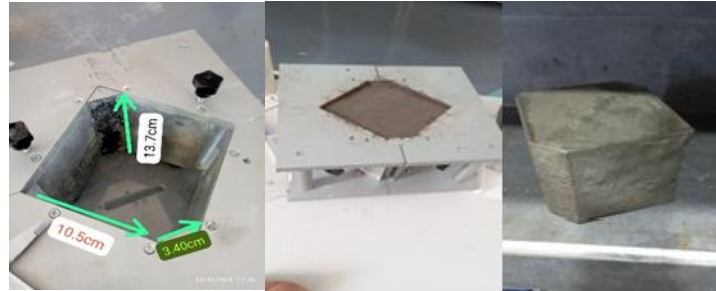


Fig 33. Mold for the triaxial test

5.4 Vcat & Consistance Test

The Vicat test determines the normal consistency as well as the initial and final setting times of our cement paste. It allows us to evaluate the behavior of cement in the presence of water and to monitor its evolution from a plastic to a hardened state. The consistency test determines the amount of water required to obtain a cement paste of normal consistency. This consistency is achieved when the Vicat piston penetrates the paste (see Figures 34 and 35) to a defined distance from the bottom of the mold, in accordance with the requirements of the applicable standards (EN 196-3 or ASTM C187).

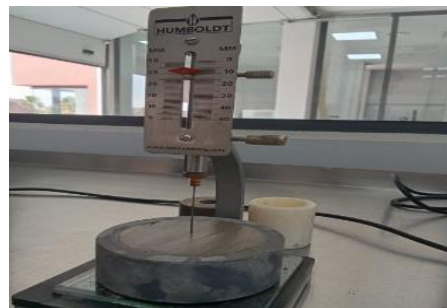


Fig 34. Manual Consistency Apparatus



Fig 35.Vcat Apparatus

Once the normal consistency has been determined using a manual consistency tester, the Vicat test is performed to measure setting times (see Table 19) using the Vicat reference apparatus Vicat matest-

Vicatronic (*Figure 35*). The Vicat needle allows for the identification of the initial setting time, corresponding to the point where needle penetration is partially impeded, and the final setting time (*Table 10*), when the needle no longer leaves a visible indentation on the paste surface. These parameters are essential for evaluating the material's suitability for placement and hardening under a penetration mode of 10.00 s (*Figure 36*). The Vicat and consistency tests provide fundamental information on the hydration kinetics, workability, and compatibility of the mineral admixtures, in this case natural phosphate and clay, with the cementitious binder (in this test, the sand is removed in accordance with applicable standards). This test is particularly important for the development of innovative concretes and environmentally friendly cementitious materials.

Table 19. Measurement of the penetrations numbers with the last and maximum penetration

Penetrations	86
Last penetration	28.98 mm
Maximum penetration	40.54 mm

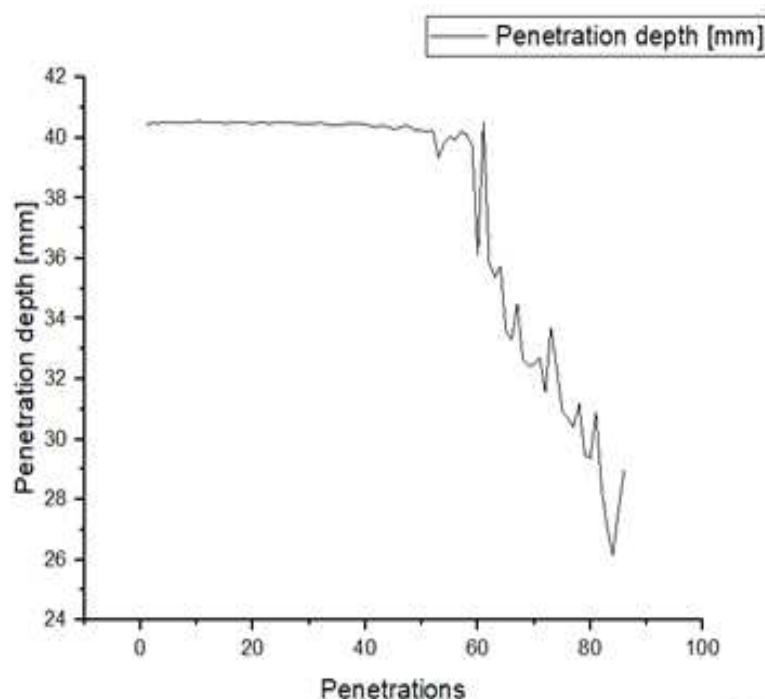


Fig 36. Evolution of penetration depth as a function of penetration for default penetration time: 10.00 sec

The VICAT penetration test reveals a decrease in penetration depth from 42 mm to 24 mm, demonstrating the progressive development of a structured particle network. This means that the initial state of the material is sufficiently fluid for easy extrusion, while its higher consistency at the end of preparation ensures excellent dimensional stability of the printed layers. This optimal balance between fluidity during extrusion and stability after deposition is essential for 3D printing.

5.5 Reology Test

The rheological properties of the paste mixture evaluated in its fresh state to characterize its flow behavior. This behavior determines the material's ability to flow under stress while maintaining its stability after deposition, as well as its workability. These tests allow for the analysis of fundamental parameters such as yield stress (*Figure 40*), plastic viscosity, and thixotropy (*Figures 38, 39, and 40*). The workability and fluidity of the concrete under its own weight are also evaluated. The average spread diameter is measured after cone removal, providing an overall indication of the material's fluidity.



Figure.37 Rehometer (RheoCompass)

Rheological measurements were performed using a concentric-cylinder measuring geometry (CG27, Anton Paar, part no. 78234). The inner measuring cylinder had an effective length of 40.008 mm and a diameter of 26.656 mm, while the outer cup had a diameter of 28.909 mm. The system had a nominal end-effect correction factor of 1.1. According to the manufacturer's specifications, the measuring geometry supports rotational speeds up to 3000 rpm and temperatures ranging from -40 to 300 °C. These tests are particularly relevant for detecting blockage or segregation phenomena. Instrumented rheological characterization is performed using a rheocompass rheometer, the reference rheometer MCR 302e (Figure 39), which measures the relationship between shear stress and shear rate. The results are interpreted using rheological models such as the Bingham model (Figure 41) to determine the yield stress and plastic viscosity of the material. Specifically, the following graphs are used: regression threshold, Bingham model, hysteresis area as a function of viscosity, shear gradient as a function of shear rate, standard smoothing, log-log smoothing with a relative range of 3%, and viscosity as a function of the shear gradient in s^{-1} . The thixotropy of concrete is evaluated by shear cycles or shear-remainder tests, highlighting the evolution of the internal structure of the material as a function of time and applied shear.

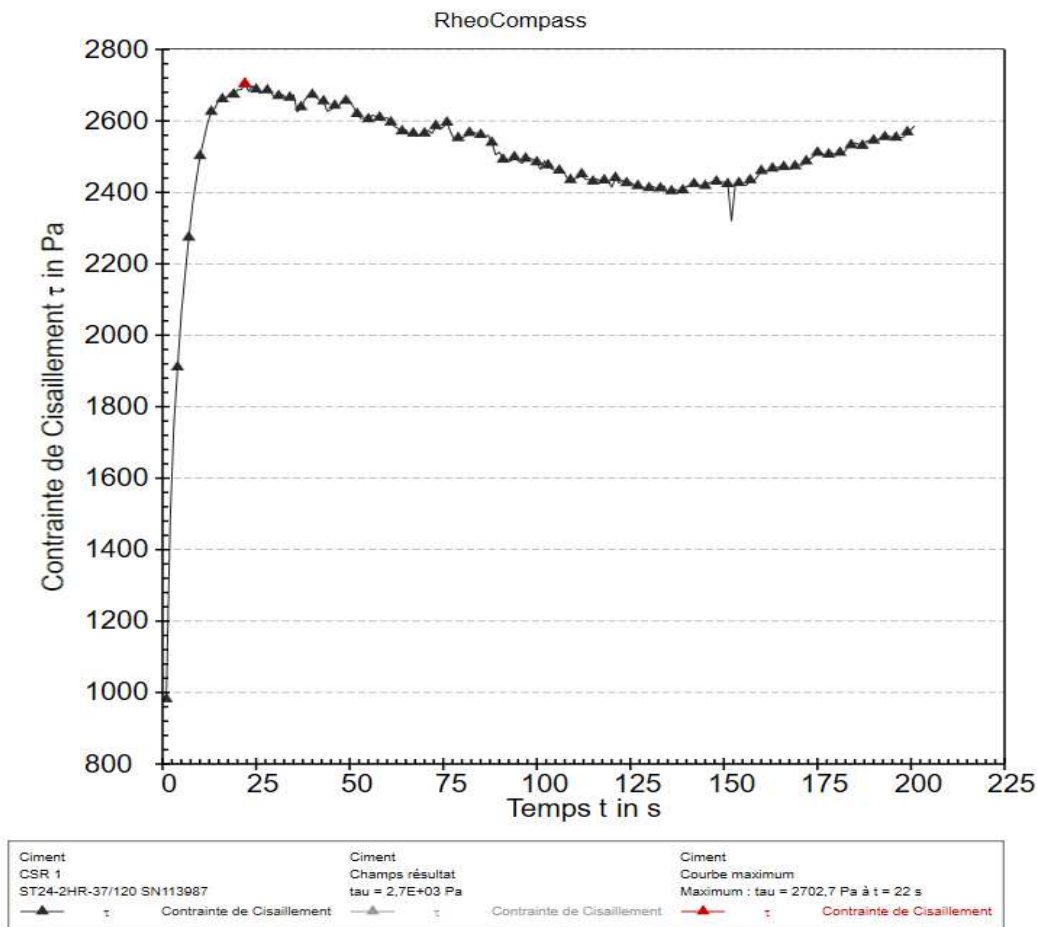


Fig 38. Calculation of the shear stress τ in (Pa) as a function of time (s)

Figure 38 represents this maximum: $\tau = 2702.7 \text{ Pa}$ at $t = 22 \text{ s}$, the material therefore very quickly reconstitutes a solid network; the thixotropy is very strong and the material remains very rigid and elastic even after a short pause.

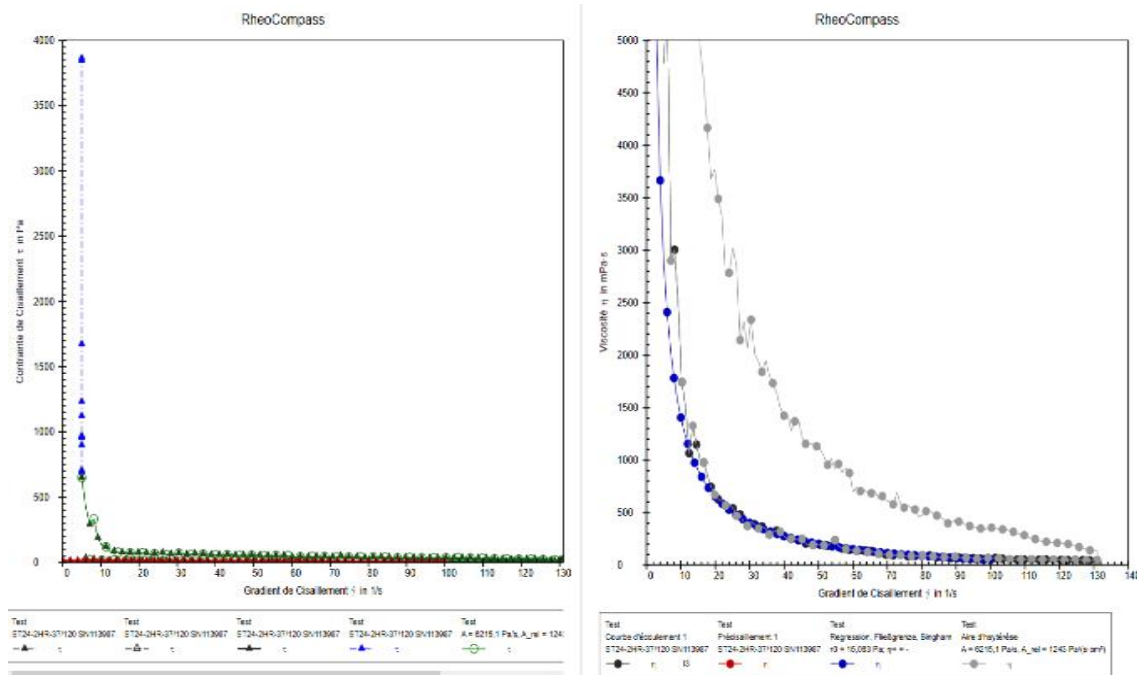


Fig 39. a) Shear stress τ (Pa) as a function of the shear gradient $\dot{\gamma}$ (s^{-1}) b) Flow curve with hysterical air, regression, Fliebgrenze, Bingham.

Figure 39 represents the yield stress (τ_0), the minimum stress required to initiate flow. It is directly related to the internal particle network and interparticle interactions.

- A high value of τ_0 , equal to 5,000 Pa, indicates good paste stability at rest. The viscosity decreased from $1.3 \times 10^5 \text{ mPa}\cdot\text{s}$ at the first measurement point to $142 \text{ mPa}\cdot\text{s}$ at the final measurement point. The regression analysis yielded a yield stress (τ_0) of 15.063 Pa, while the infinite-shear viscosity (η_∞) could not be determined. The hysteresis loop area was 6215.1 Pa/s, with a relative hysteresis area (A_{rel}) of $1243 \text{ Pa}/(\text{s}\cdot\text{cm}^3)$, indicating time-dependent changes in the flow behavior of the material under the applied shear conditions.

Based on the linear evolution of shear stress as a function of the shear rate beyond the yield stress, the rheological behavior of the material can be adequately described by the Bingham model. This model offers a simplified yet effective description of the rheological behavior of cementitious materials, making it suitable for process control and numerical simulation in 3D extrusion printing. The yield stress also represents the minimum shear stress required to initiate flow, reflecting the strength of the internal particle network.

- A high shear stress yield stress ensures good stability at rest and high load-bearing capacity for printed sofas. Regression analysis of the flow curves allows for the quantification of rheological parameters and the evaluation of the suitability of different constituent models. A good regression (high R^2) indicates a suitable model and low deviation, and therefore reproducible behavior. The shear stress is intermediate to high ($\dot{\gamma} = 10\text{--}130 \text{ s}^{-1}$). Density stabilization corresponds to the partial destruction of the crystalline lattice, which is maintained in equilibrium. The material behaves like a quasi-stable Bingham fluid, allowing for continuous and homogeneous flow. This plate is ideal for 3D extrusion because it guarantees a constant viscosity in the nozzle. The viscosity plate indicates that the material has achieved a constant shear flow, thus ensuring smooth extrusion without abrupt flow variations.

❖ Viscoelastic moduli (G' and G'') :

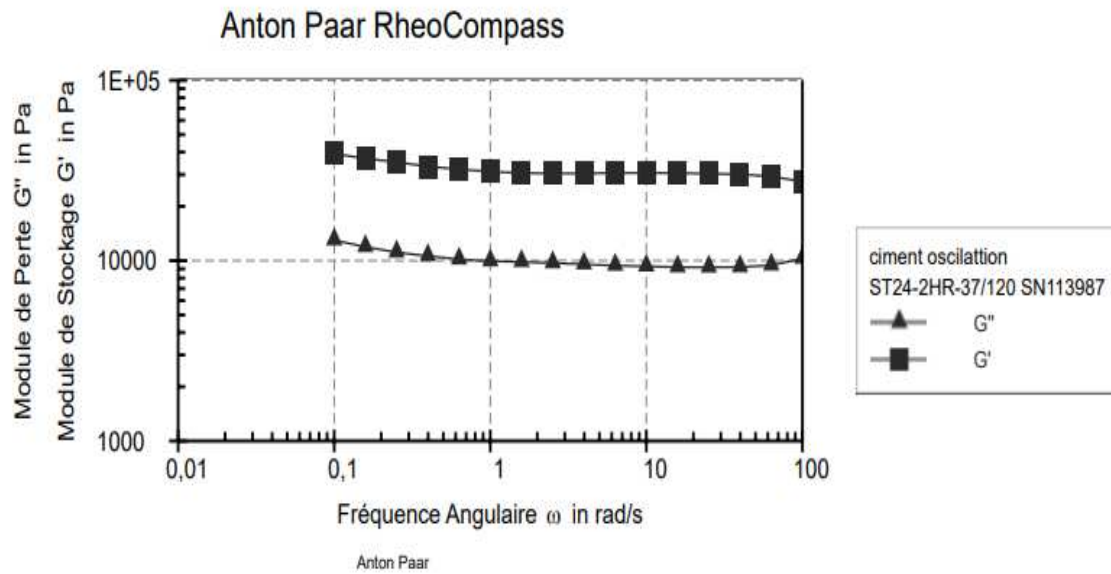


Fig 40. Loss modulus G'' in Pa and storage modulus G' in Pa as a function of angular frequency ω in rad/s

Based on the results shown in Figure 40, which illustrates the oscillation of the paste, the predominance of the storage modulus (G') over the loss modulus (G'') suggests solid-like behavior, confirming the presence of a structured particle network.

Since $G' > G''$, this is therefore a structured material exhibiting good geometric stability.

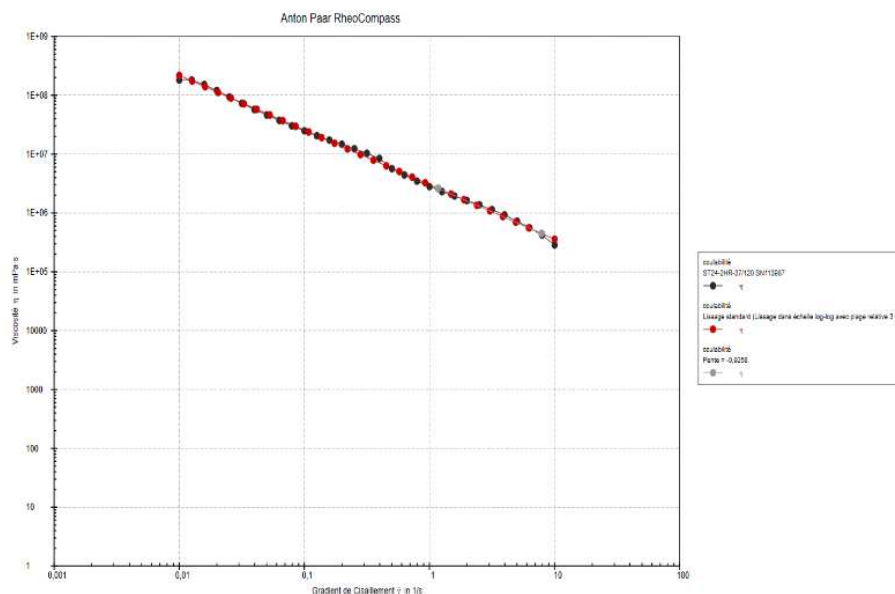


Fig 41. Complex viscosity (η) in Pa.s and loss factor $\tan \delta$ (&)

The apparent viscosity decreases with increasing shear rate, indicating a pronounced shear-thinning behavior. This non-Newtonian behavior is advantageous and perfectly suited to 3D printing of concrete, as it allows for fluid extrusion under high shear while maintaining sufficient rigidity once the material is deposited.

In conclusion, after all these rheological tests, the validated and obtained rheological properties demonstrate that the formulated material meets the essential requirements of 3D printing of concrete by extrusion, particularly in terms of pumpability, formability, and shape retention.

5.6. Particle Size Analysis par laser

Laser particle size analysis, performed using the MASTERSIZER 3000, determines the particle size distribution (PSD) of powders or suspensions. For phosphate waste, it helps assess fineness and homogeneity, optimize powder properties for 3D printing, and control reactivity, flowability, and compaction density. A laser beam passes through a dispersed powder or liquid suspension (our mixture of sterile phosphate waste and red clay with cement and crushed sand) using a laser particle size analyzer (Figure 42). The proportions for the design and production of the test samples ($4 \times 4 \times 16 \text{ cm}^3$) are given in Table 20.

Table 20. Cement mixture with phosphate waste

Component	Mass (g)	Comment
CEM I 52.5	265 g	High dosage for performance
Sand 0–2 mm	150 g	Main aggregate
Phosphate waste (sludge + waste rock + gypsum)	100 g	Well ground and homogeneous
Red clay	30 g	Improves cohesion
Superplasticizer (PCE)	~7 g	Reduces water without loss of fluidity
Water (W/C ~ 0.38)	~77 g	Calculated for resistance
Total	~629 g	For a $4 \times 4 \times 16 \text{ cm}$ (256 cm^3) test tube



Fig 42. Laser particle size analysis device

5.7 Laser Particle Size Analysis – Wet Mode

Liquid laser particle size analysis (LPSA) is a technique for measuring the particle size distribution of powders or suspensions. It involves dispersing particles in a liquid medium and analyzing their scattering using a laser beam. The particles suspended in the liquid pass through this beam. The angle and intensity of the scattered light are measured and converted into a particle size distribution using optical models (Mie or Fraunhofer) (see Figure 43).

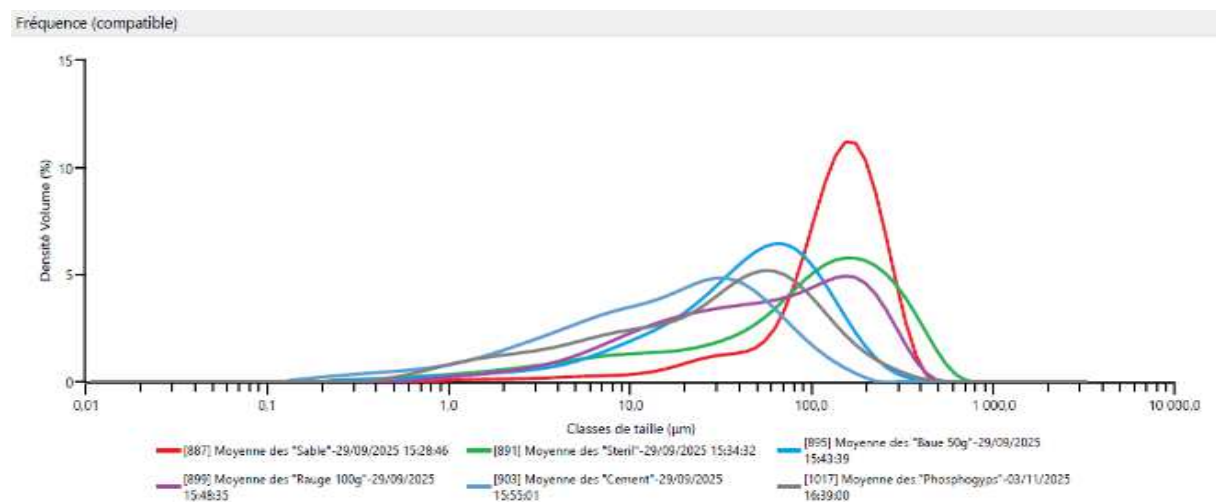


Fig 43. Laser particle size analysis of sand, cement, rock waste, sludge, and phosphogypsum Wet Mode.

Figure 43 represents the analysis of the laser particle size of sand, cement, rock waste, sludge and phosphogypsum in wet mode.

5.8 Laser Particle Size Analysis – Dry Mode

The dry mode measures particle size by dispersing powder directly into air (without liquid) and passing it through a laser beam. The dry particles are transported by compressed air or under vacuum to the path of the laser beam. The scattered light is analyzed to determine the particle size distribution (see Figure 44).

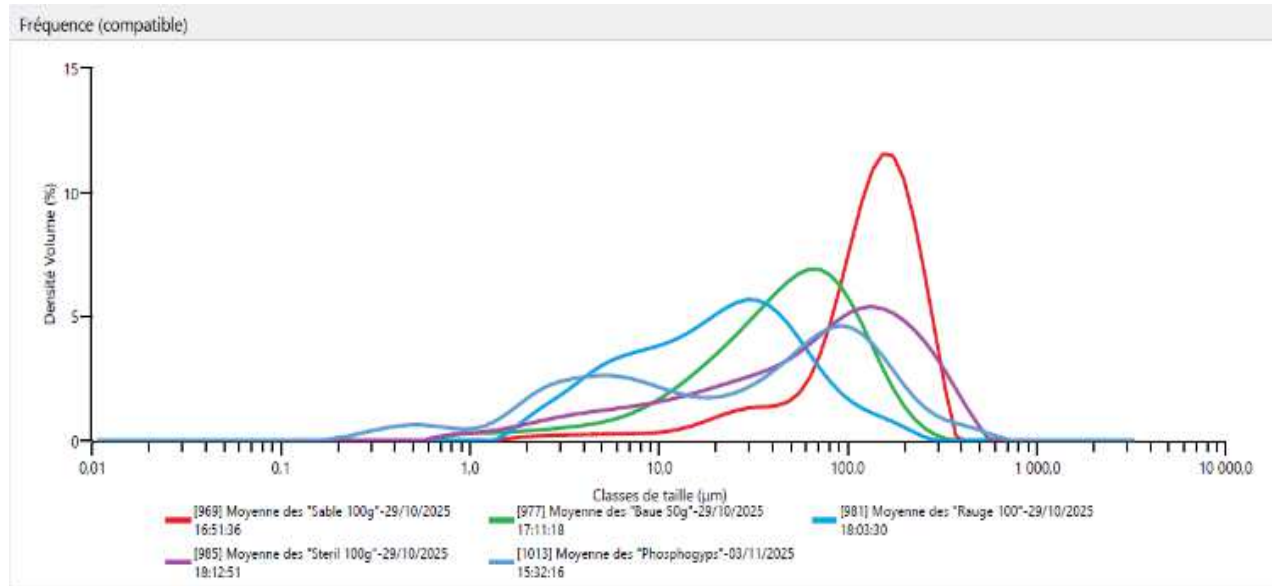


Fig 44. Laser particle size analysis of sand, cement, rock waste, sludge, and phosphogypsum Dry Mode

In the figure 44 represent Laser particle size analysis of sand, cement, rock waste, sludge, and phosphogypsum in Wet Mode.

6. Morphology (SEM)

The morphology of the cementitious mixture was studied by scanning electron microscopy (SEM) to analyze its microstructural characteristics and the distribution of hydration products. SEM observations were performed on fractured and dried samples to preserve the internal microstructure of the material. SEM imaging was carried out at different magnifications to examine the surface texture (Figures 45, 49, and 52), the porosity structure, crack networks, and the morphology of the hydration products. SEM analysis made it possible to identify characteristic phases such as calcium silicate hydrates (C-S-H) (see the three spectra) (Figures 45, 46 and 47) and to evaluate the interfacial adhesion between the cementitious matrix and the added materials.

6.1 Microstructural Analysis (SEM) – Powder State

A ThermoFisher Apreo 2S reference scanning electron microscope (SEM) is used to analyze the microstructure, morphology, and surface characteristics of phosphate waste powder mixtures. This analysis allows for the examination of particle shape and size, the identification of surface texture, porosity, and agglomeration, and, most importantly, the evaluation of their suitability for 3D printing.

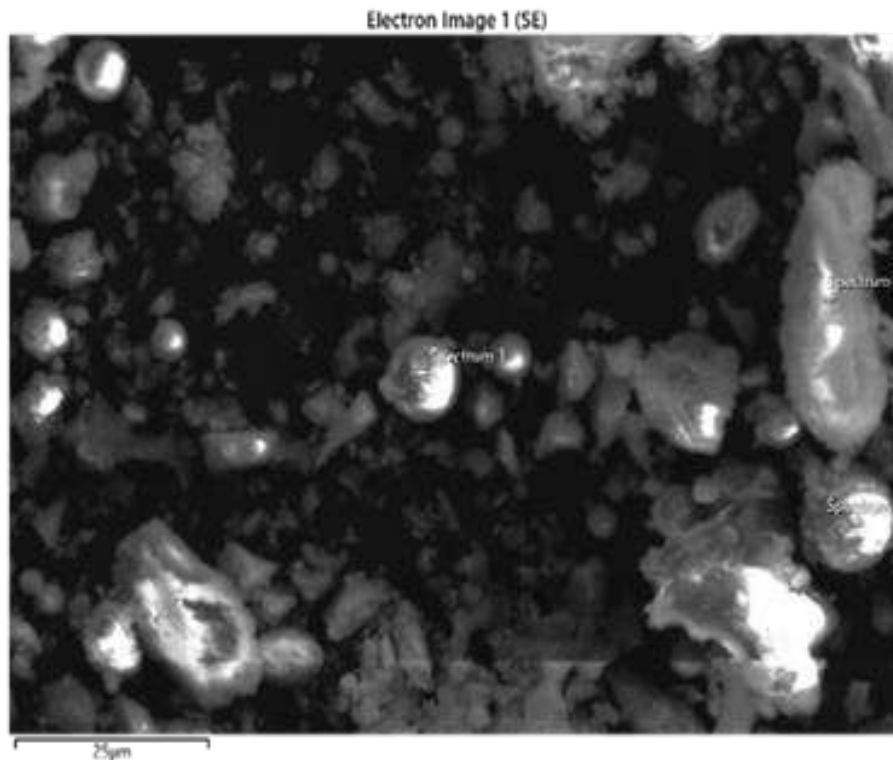


Fig 45. SEM test of the powder mixture

In Figure 45 Examine the shape and size of the particles in the powder mixture (composition of sterile sand, cement, red clay, crushed sand in dry state).

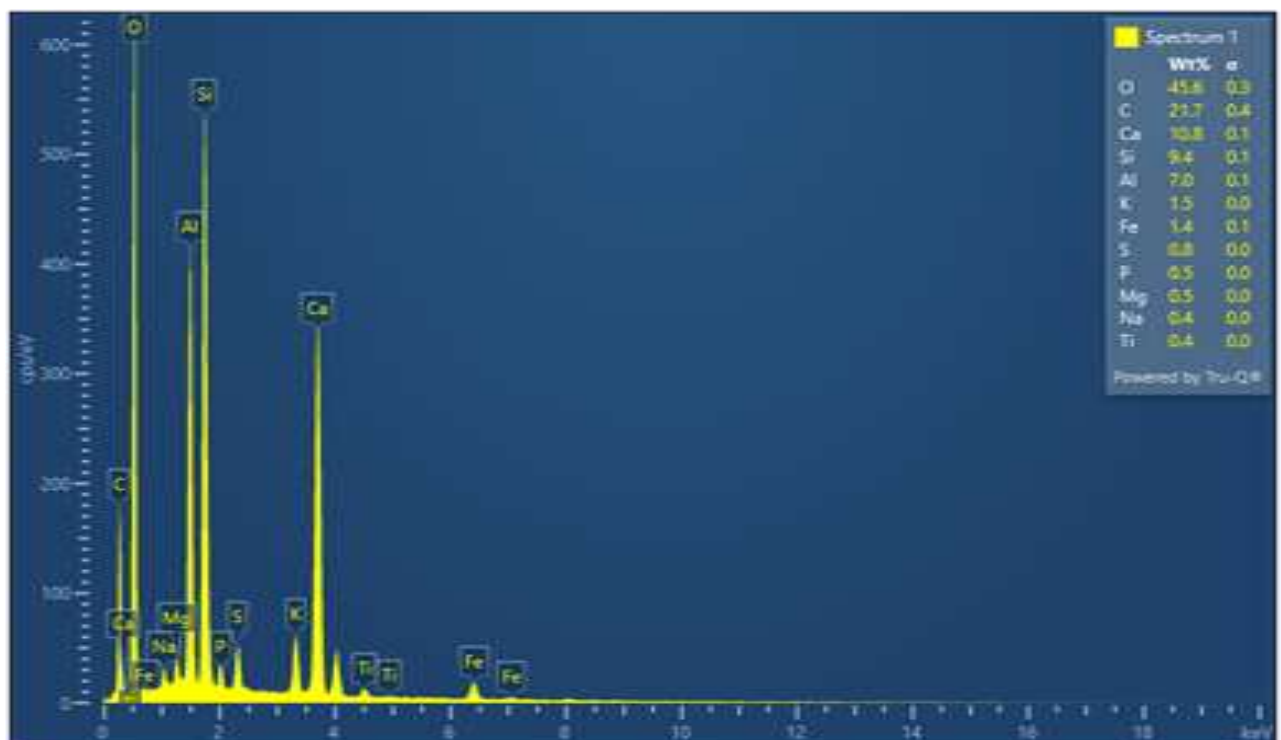


Fig 46. SEM test of the powder mixture (electron image, spectrum 1)

In figure 46 represent SEM Test in spectrum 1, represent 45.6% O, 21.7% C, 10.8% Ca, 9.4% Si, 7.0% Al, 1.5% K, 1.4% Fe, 0.8% S, 0.5% P, 0.5% Mg, 0.4% Na, 0.4% Ti.

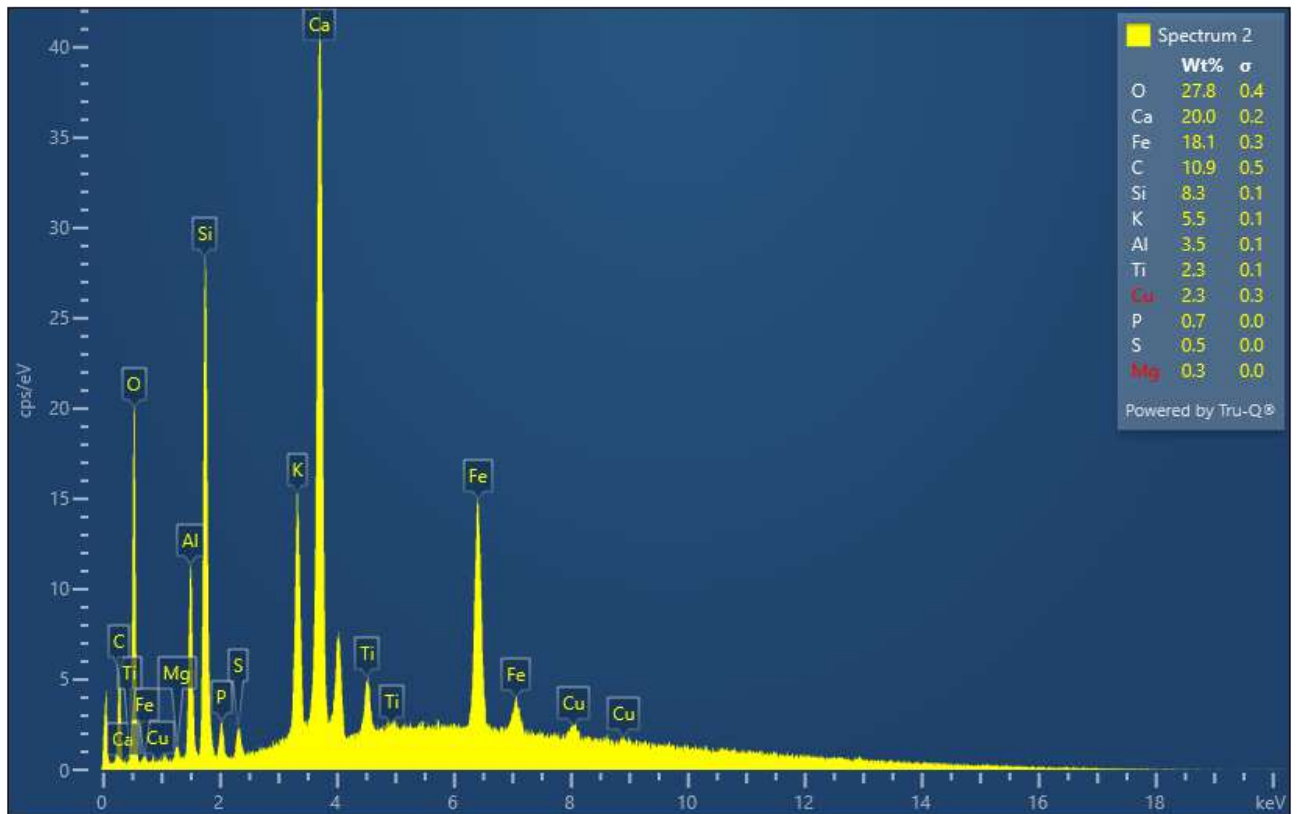


Fig 47. SEM test of the powder mixture (electron image, spectrum 2).

In figure 47 represent SEM Test in spectrum 2, represent SEM Test Represented in spectrum 2, 27.8% O, 20.0% Ca, 18.1% Fe, 10.9% C, 8.3% Si, 5.5% K, 3.5% Al, 2.3% Ti, 2.3% Cu, 0.7% P, 0.5% S; 0.3% Mg.

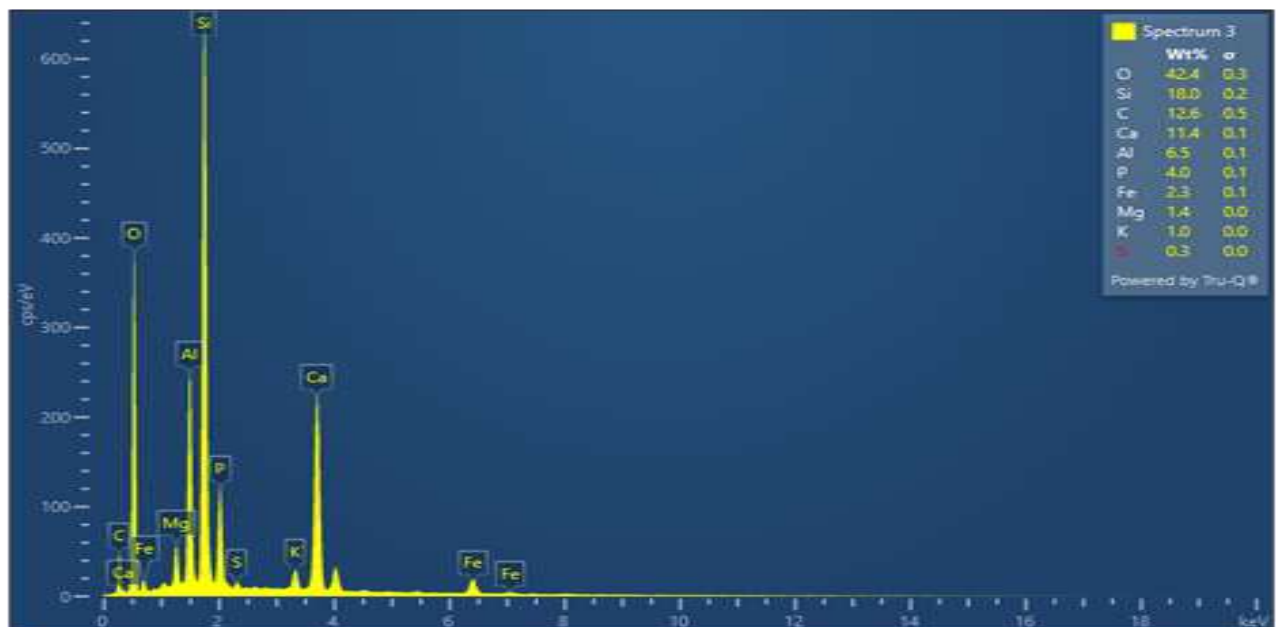


Fig 48. SEM test of the powder mixture (electron image, spectrum 3).

In figure 48 represent SEM Test, Represent in spectrum 3, 42.4% O, 18.0% Si, 12.6% C, 11.4% Ca, 6.5% Al, 4.0% P, 2.3% Fe; 1.4% Mg, 1.0% K, 0.3 S.

SEM images of the phosphate waste reveal irregular, angular particles of heterogeneous size and a rough surface texture. The presence of pores and agglomerates indicates the complexity of the raw material. EDS analysis confirms the presence of major elements such as calcium, phosphorus, and oxygen, characteristic

of phosphate minerals, as well as minor elements like silicon, aluminum, and magnesium, typical impurities in phosphate waste. The combined SEM and EDS results indicate a heterogeneous phosphate-based material containing mineral impurities, consistent with the nature of industrial phosphate waste. These characteristics suggest that the phosphate waste has strong potential as a secondary raw material for the development of environmentally friendly composites and 3D printing materials, after appropriate processing and formulation.

6.2 Specimen with 160 g of water- Test Morphology SEM After 28 days

In this section, a morphological test was carried out on samples of the M2-65 mixture, composed of 100 g of sterile, 30 g of red clay and 265 g for cement type C65, with a water content of 160 g. This sample was chosen for its high resistance, achieved at: 46,528 MPa.

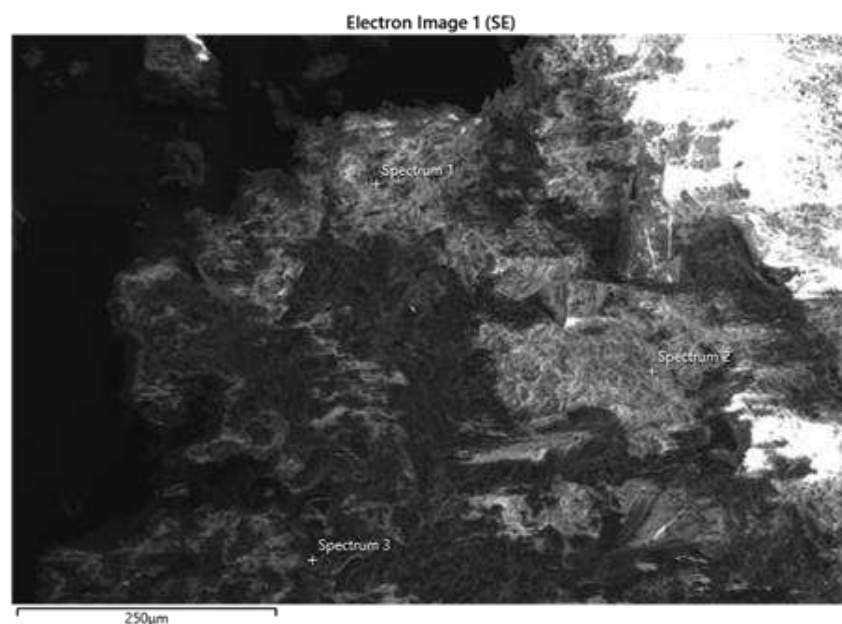


Fig 49. SEM test of the specimen Test with 170 g of water (electron image, spectrum 1, spectrum 2, spectrum 3).

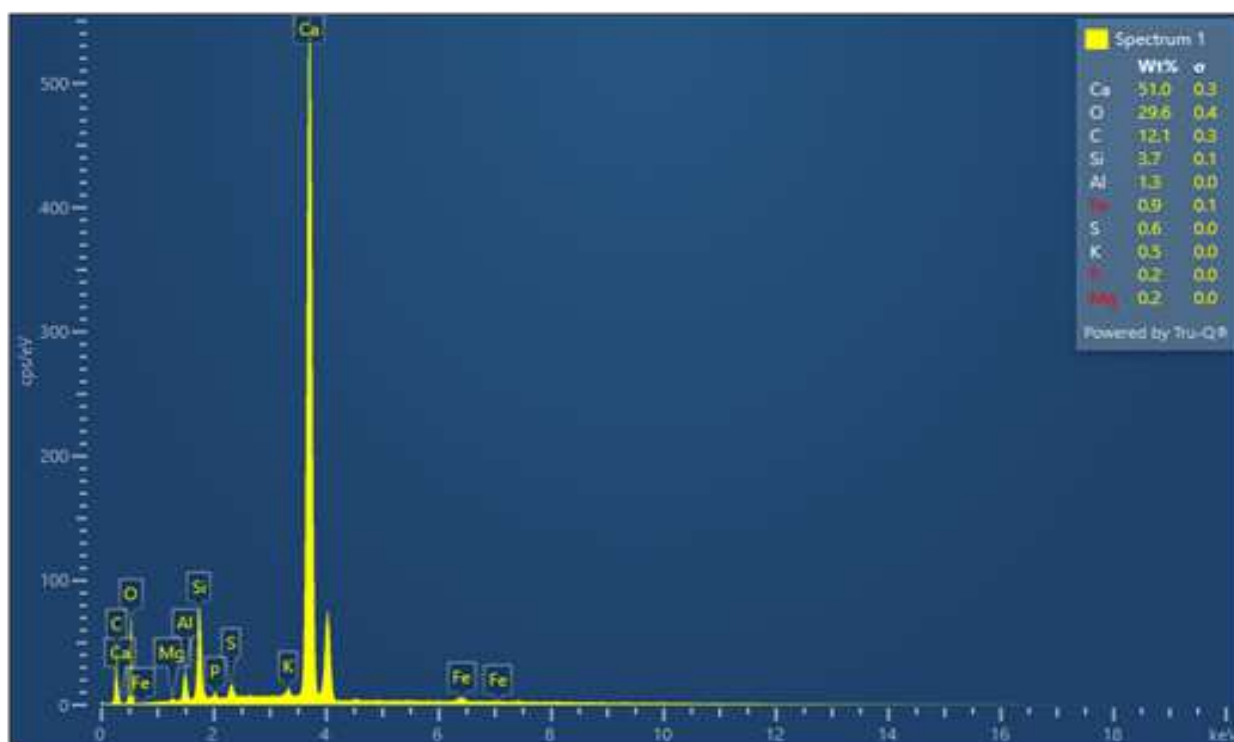


Fig 50. SEM test of the specimen with 170 g of water (electron image, spectrum 1).

SEM Test Represent in spectrum 1, 51.0% Ca, 29.6% O, 12.1% C, 3.7% Si, 1.3% Al, 0.9% Fe, 0.6% S, 0.5% K, 0.2% P, 0.2 Mg.

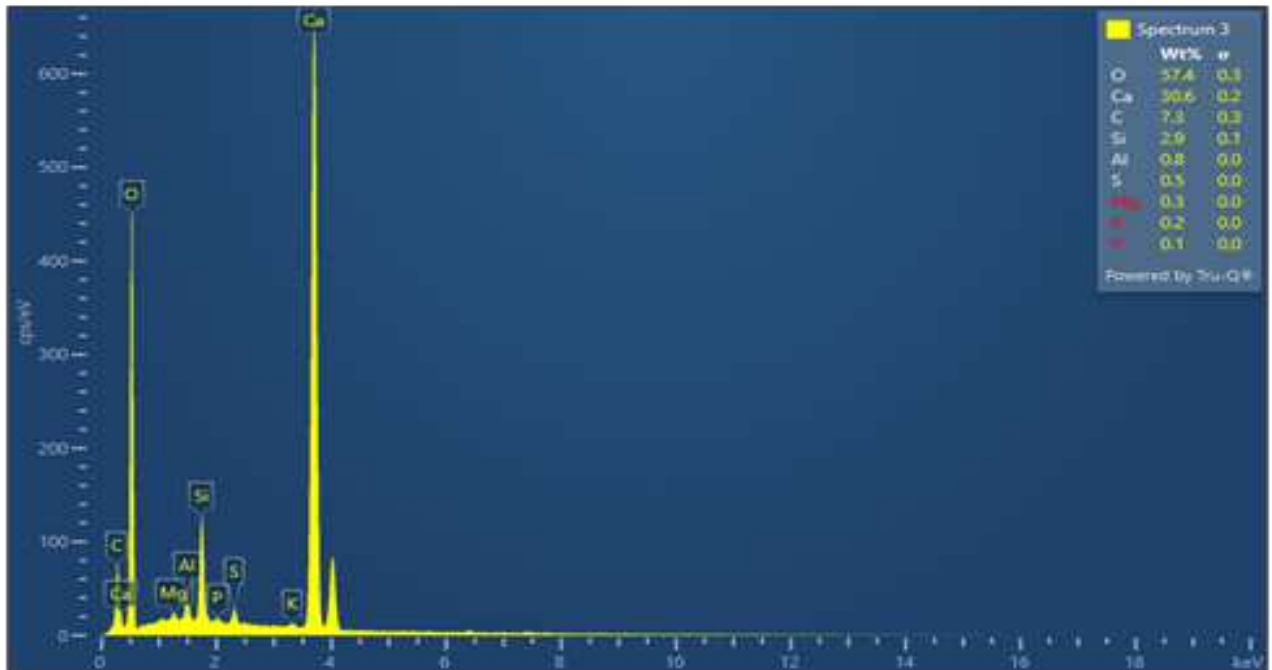


Fig 51. SEM test of the specimen Test tube with 170 g of water (electron image, spectrum 3).

SEM Test Represent in spectrum 3, 57.4% of O, 30.6% of Ca, 7.3% C, 2.9% Si, 0.8% Al, 0.5 S, 0.3 Mg, 0.2 K, 0.1 P. Calcium, oxygen, carbon, silicon, aluminum, iron, sulfur, potassium, phosphorus, magnesium: these are all chemical elements present in our cementitious materials made from phosphate waste and red clay. K, Mg, and P are present in trace amounts in the phosphate waste.

6.3 Specimen with 145 g of water after 28 days

This second test, carried out with the same mixture but with a reduced water content of 145 g, was performed on samples of the M1- 45 mixture, composed of 100 g of sterile cement, 30 g of red clay and 265 g of C45 cement. This sample was chosen for its high resistance, on the order of 32,123 MPa, for this type of cement.

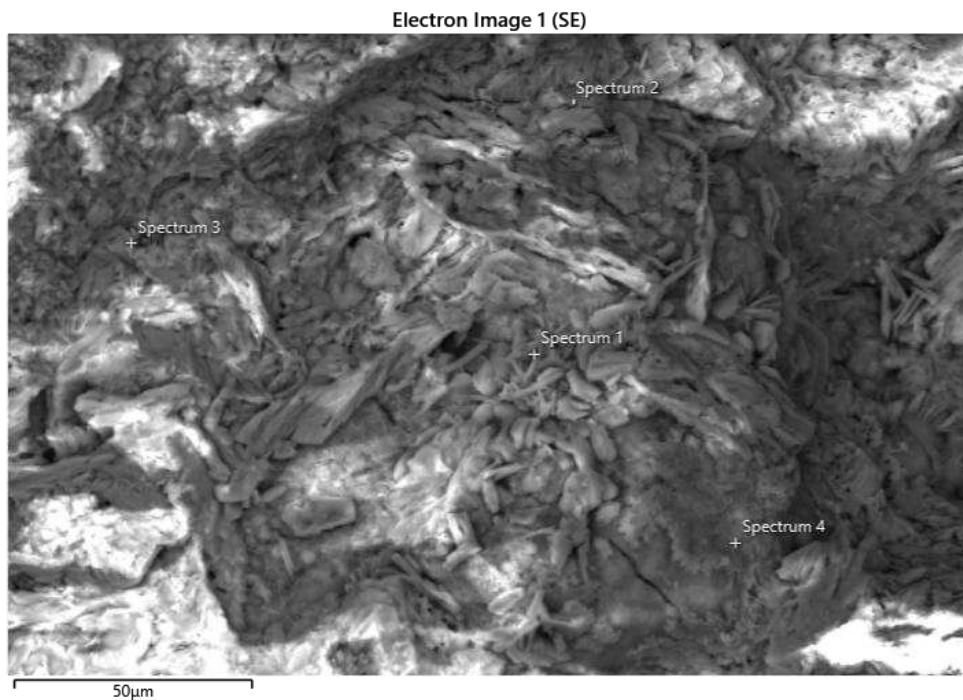


Fig 52. SEM test of specimen with 145 g of water

The figure 52 represent SEM test of specimen with 145 g of water (electron image, spectrum 1, spectrum 2, spectrum 3, spectrum 4).

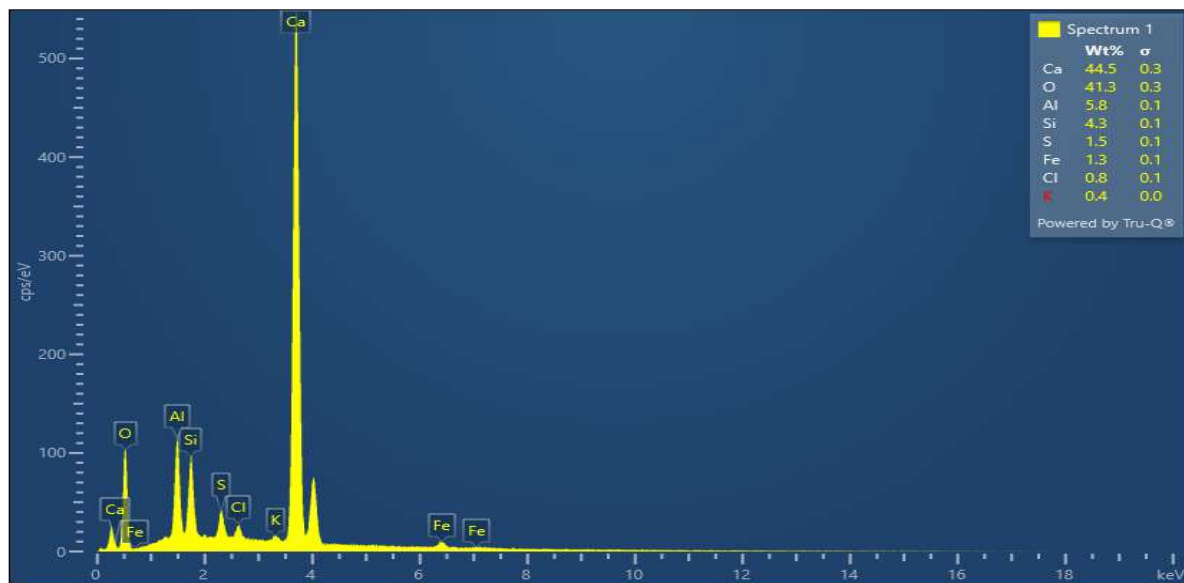


Fig 53. SEM test of the specimen with 145 g of water (electron image, spectrum 1).

The figure 53 represent SEM Test spectrum 1, 44.5% of Ca, and 41.3% of O, and 5.8% of Al, 4.3% Si, 1.5% S, 1.3% Fe, 0.8 Ci, and 0.4 K.

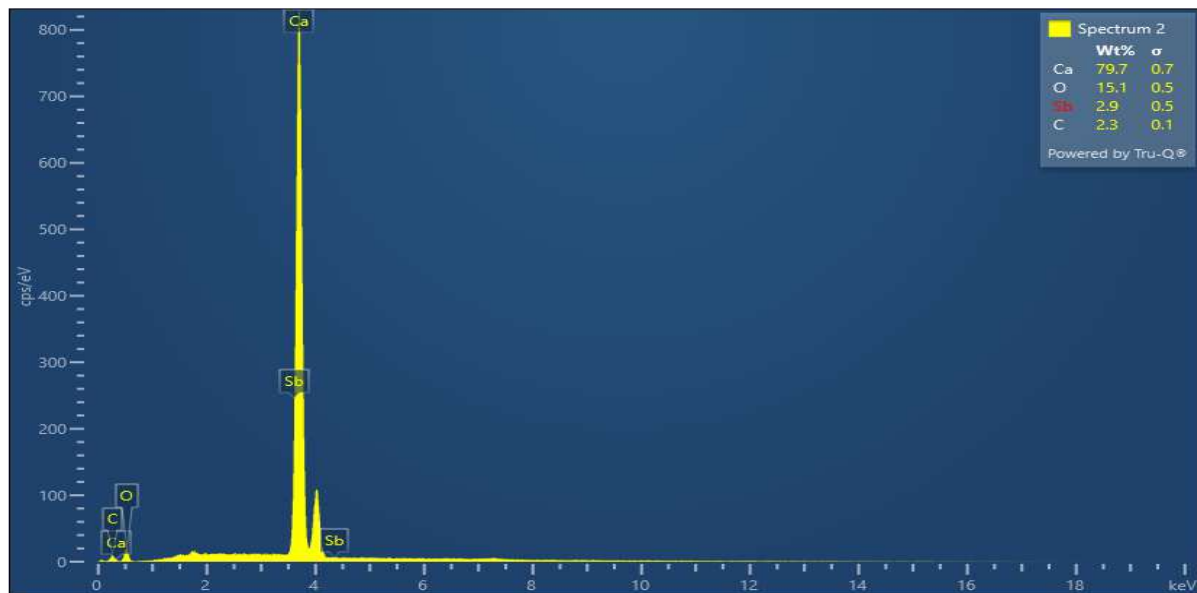


Fig 54. SEM test of the sample Test tube with 145 g of water (electron image, spectrum 2).

The figure 54 represent SEM Test spectrum 2, 97.7% of Ca, and 15.1% of O, and 2.3% of C, 2.9% Sb.

Conclusion

This study investigated the incorporation of Moroccan phosphate-industry by-products into cementitious mixtures containing local red clay and crushed sand, with a view to exploring their potential for future 3D concrete printing applications. The experimental program examined the physicochemical characteristics of the constituent materials, particle-size distribution, morphology, mechanical performance, and rheological behavior of the developed mixtures. The results showed that the mechanical and rheological properties varied according to the cement type, water content, and proportions of the constituent materials. The maximum reported compressive strengths reached 21.877 MPa, 32.123 MPa, and 46,528 MPa for mixtures prepared with C25, C45, and C65 cement, respectively. These findings indicate that the incorporation of phosphate-industry by-products into cementitious formulations warrants further investigation, although the contribution of the waste materials to the observed performance requires more rigorous comparison using reference mixtures with comparable compositions. From a resource-efficiency perspective, the use of phosphate-industry by-products in construction materials represents a potential valorization pathway that could contribute to reducing the accumulation of industrial residues and supporting circular-economy initiatives. However, the environmental benefits and safety of the developed mixtures cannot be established from the present results alone. Further investigations are required to assess trace-element leaching, radiological characteristics, and environmental performance. Moreover, although the measured mechanical and rheological properties provide a basis for further development, the suitability of the mixtures for extrusion-based 3D concrete printing has not yet been experimentally demonstrated. Future work should therefore focus on direct printing trials, including extrudability, buildability, layer stability, interlayer bonding, and dimensional accuracy. Improved mixture-design procedures, systematic replication, statistical analysis, and comprehensive characterization of the raw materials are also necessary to establish reliable relationships between composition and performance. Overall, this study provides an experimental starting point for investigating the valorization of Moroccan phosphate-industry by-products in cementitious materials and identifies research directions for evaluating their potential in additive construction manufacturing.

Nomenclature

XRD: X-ray Diffraction

SEM: Electron Microscopy

XRF: X-ray Fluorescence

APS: Laser Particle Size Analysis

VPS: Specific Pore Volume

TGA: Thermogravimetric Analysis

LFA: Laser Flash Analysis

PG: Phosphogypsum

C25: Concrete class with a compressive strength of 20 MPa after 28 days, used for non-load-bearing or lightly loaded structures.

C45: Concrete class with a compressive strength of 45 MPa after 28 days, used for highly loaded structures such as beams, slabs, columns, and prestressed structures.

C65: Concrete class with a compressive strength of 65 MPa after 28 days, used for very demanding and technical structures such as large bridges, prestressed buildings, towers, or industrial structures subjected to heavy loads.

3D: Three-dimensional

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Declaration of Conflicts of interest

The author declare that there is no conflict of interest.

Availability of Data and Materials

Data will be made available on request.

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