RECYCLING OF FLINT FROM PHOSPHATE WASTE ROCKS TO PRODUCE CEMENT MORTARS

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Summary

The extraction, processing, and beneficiation of phosphates generate significant amounts of waste rocks, posing potential environmental issues such as land disfiguration and the loss of arable land. On the other hand, the construction industry contributes substantially to the depletion of natural resources, particularly sand. This paper explores a novel approach to address these challenges by proposing a circular economy solution that involves repurposing waste rock materials for construction industry applications. This study focuses on evaluating the feasibility of using Waste Flint (WF) from Phosphate Waste Rocks (PWR) as an alternative fine particle to 100% replace manufacturing sand (MS). However, the acceptance of WF as an alternative sand depends on its effective properties. In this regard, various tests have been conducted to investigate the impact of WF on the properties of cement mortar. The findings reveal that WF-mortar exhibits lower density, higher water absorption, lower compressive strength, and lower flexural strength at early ages, but it demonstrates good resistance to flexural stress at later ages. XRD analysis confirmed that WF has no adverse effect on the formation of hydration products in cement paste. Moreover, WF contributes to the formation of a denser Interfacial Transition Zone (ITZ) with the cement paste. Based on this, it is recommended to explore the partial replacement of MS with WF for further enhancement of the cement mortar properties. This research offers a promising route for sustainable waste utilization in the construction industry within the framework of a circular economy.

1 INTRODUCTION

Morocco is recognized for englobing the world's largest phosphate reserves, concentrated within four sedimentary basins in the country. Together, these basins hold approximately two-thirds of the global phosphate reserves [1]. The recent population growth aligns with an increased demand for agriculture and fertilizer production, where phosphorus ores play a vital role [2]. However, during the extraction and processing of this mineral, huge amounts of mine waste rocks are generated and often improperly disposed of on the mine surface due to the deep location of phosphate ore layers [3]. Although these mine wastes are chemically inert, their improper storage negatively impacts the environment, leading to environmental issues like land disfigurement and loss of arable land [4]. The effective utilization and proper management of these mine wastes present an opportunity to contribute to environmental protection while maintaining economic benefits [5]. Researchers are currently exploring the recycling of these wastes to create eco-friendly products for various applications, particularly in the construction sector, involving cement [6], geopolymer [7], brick [8], [9], and concrete [10], [11].

On the other hand, in Morocco, river sand is a fundamental source for preparing construction mortar. With the rapid growth of the construction industry, there has been a substantial surge in the demand for river sand. This large demand has led to the utilization of crushed sand, sourced from the crushing of rock layers from quarries as an alternative. However, this shift has resulted in an increase in construction costs. The extraction of river sand and manufacturing sand is also contributing to environmental concerns, causing riverbed deepening, deterioration of channel morphology and the loss of vegetation along riverbanks [12].

This paper explores a novel approach towards an effective solution for these challenges by integrating a circular economy solution that involves repurposing these waste rock materials for construction industry applications. In response to these challenges, we suggest the recycling of waste flint taken from intercalation layers of phosphate in the Gantour basin, Morocco as fine aggregates to replace manufacturing sand in cement mortar production totally. Consequently, the use of waste flint as fine aggregates in cement mortar production can help reduce the need for natural sand and manufacturing sand used as construction materials. Moreover, this solution can provide a cost-effective solution for managing the phosphate mine waste while promoting sustainable practices in the civil engineering sector.

2 EXPERIMENTAL WORK

2.1 Raw materials

Waste flint used in this study was collected from the phosphate interlayers of the Gantour basin, Benguerir phosphate mine ***Figure 1*** (a). The flint blocks were crushed, sieved through a 5 mm sieve, and then dried at 105 ± 5 ºC until a constant weight was achieved ***Figure 1*** (b). River sand was used as a reference alongside ordinary Portland cement (CPJ-45), used as a binder, and tap water without any other additives.

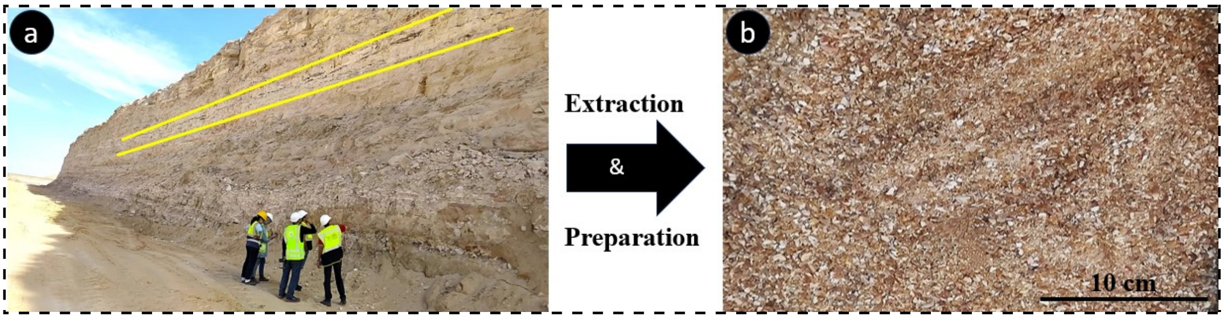

Figure 1. (a) Position of flint sand within intercalation layers of phosphate; b) flint sand post crushing and sieving procedure.

2.2 Mixing design

Table 1 presents the mixture proportions of reference mortar and WF-mortar. For this study, a Sand:Cement:Water ratio of 3:1:0.5 by mass was used to prepare mortar mixes. An automatic planetary mixer was employed for the experimental mixing process. Initially, the mixer received water and cement, completing the mixing operation within 1 min. Subsequently, sand was gradually introduced over the next 1 min. An additional minute of mixing was devoted to the cement mortar. The entire mixing process was extended for an extra 7 min, ensuring that the cumulative mixing time for all mortar variations remained within the 10 min limit. The resulting mortar specimens were then cured in a water bath at ambient temperature until the testing time [13].

Table 1. Mix proportions of MS-mortar and WF-mortar.

Sample	WF (g)	MS (g)	Cement (g)	water (g)	w/c
MS-M	0	1350	450	225	0.5
WF-M	1350	0	450	225	0.5

2.3 Experimental techniques

Physical and geotechnical characteristics of WF were tested following different specifications, including particle size distribution (NM EN 933-1), apparent density (NM EN 1097-3), Sand equivalent (NM EN 933-8), water absorption (NM EN 1097-6), water content (NM EN 1097-5) and fineness modulus (NM EN 933-1). Chemical and mineralogical compositions were analyzed with X-ray fluorescence (Epsilon 4 Model to determine the elemental composition of raw materials, Malvern Panalytical) and Bruker-AXS D8 X-ray diffraction pattern apparatus with Cu Kα radiation ($\lambda k\alpha$ = 0.154186 nm at 40 kV and 40 mA) to explore the crystalline phases present in sands and elaborated mortars in the range of 10° to 70° (2θ).

For hardened mortars, several properties were tested according to specific standards including compressive strength and flexural strength at 7 and 28 days (NM 10.1.005), dry bulk density, and water absorption at 7 and 28 days (BS EN 12390-7).

3 RESULTS AND DISCUSSIONS

3.1 Raw materials characteristics

Figure 2*. Particle size distribution of MS and WF.* illustrates the grain size distribution while ***Table 2*** presents the physical properties of both MS and WF. WF demonstrates a uniformity and classification similar to that of MS, even though it is slightly coarser. The apparent density of WF and MS are determined to be 1366.4 Kg/m^3 and 1618.2 Kg/m^3 respectively. The lower density could be advantageous in reducing the overall weight of the mortar. The

high sand equivalent (83%) qualifies WF to be classified as clean sand. This aligns with lower water content (6.54%), water absorption (4.8%), and a higher fineness modulus (3.2%) of WF, attributing to the lower fine content.

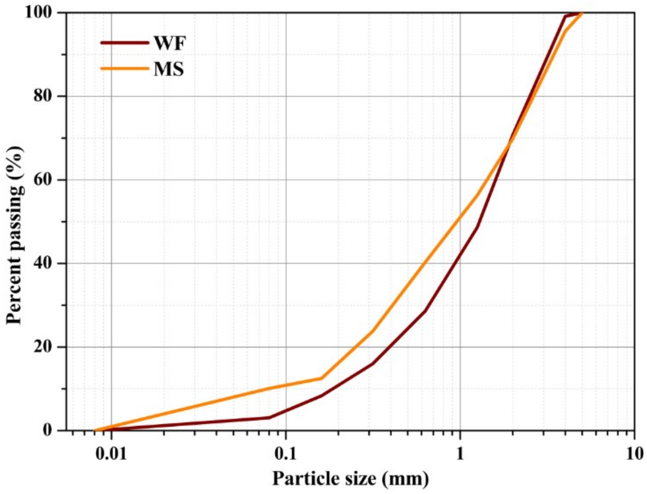

Figure 2. Particle size distribution of MS and WF.

Table 2. Physical properties of MS and WF.

Tests	Standards	WF	MS
apparent density (Kg/m^3)	NM EN 1097-3	1366.4	1618.2
Sand equivalent (%)	NM EN 933-8	83	67
Water content (%)	NM EN 1097-5	6.54	7.45
Fineness modulus	NM EN 933-1	3.20	3.11
Water absorption (%)	NF EN 1097-6	4.8	5.2

Table 3 displays the chemical composition of waste flint, manufacturing sand, and cement, whereas ***Figure 3*** presents their X-ray diffraction patterns. WF is primarily composed of SiO_2 (69.6%), CaO (15.2%), and P_2O_5 (10.5%), whereas MS consists mainly of SiO_2 (59.7%), Al_2O_3 (14.7%), Fe_2O_3 (8.79%), and K_2O (6.66%). These findings align with the XRD results, indicating the dominance of quartz (SiO_2) peaks in both samples. For WF, additional peaks indicate the presence of dolomite ($CaMg(CO_3)_2$) and fluorapatite ($Ca_5(PO_4)_3F$). In MS, the predominant peaks include quartz (SiO_2), Albite ($NaAlSi_3O_8$), Muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$) with minor peaks of Hematite (Fe_2O_3) and Anorthoclase ($(Na,K)AlSi_3O_8$).

Table 3. Chemical composition of MS, WF, and Cement (C).

	Na_2O	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**K_2O**	**CaO**	**Fe_2O_3**	**LOI**
WF	0.5	1.8	0.5	69.6	10.5	0.1	15.2	0.5	5.17
MS	1.54	1.24	14.7	59.7	0.5	6.66	2.8	8.79	3.35
C	0.30	1.06	1.15	15.06	0.23	0.63	59.98	3.95	13.21

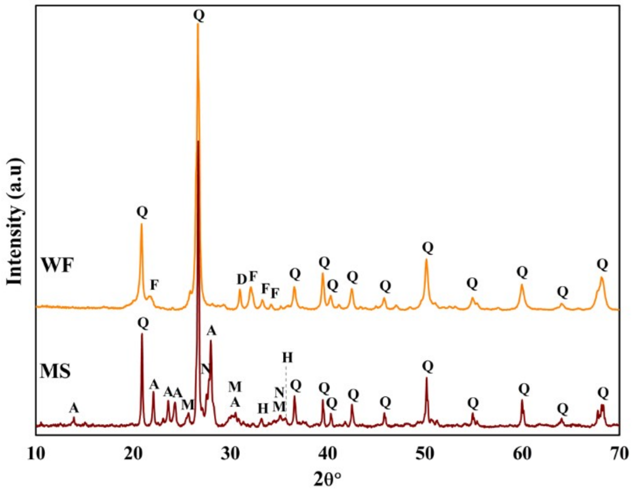

Figure 3. XRD patterns of MS and WF.

3.2 Hardened mortar characteristics

3.2.1 Dry bulk density and water absorption

Three specimens were tested to determine average values for dry bulk density and water absorption. ***Figure 4*** illustrates the influence of waste flint on the average values of dry bulk density and water absorption in mortar after 7 and 28 days of curing. Notably, WF-mortar average densities decreased at all ages compared to MS-mortar. Specifically, the density of WF-mortar decreased by 5.37% and 7.08% relative to MS-mortar at 7 and 28 days, respectively. This decline in density could be attributed to the low density of WF and the high void percentage caused by its coarse surface and angular particle shape [14], [15].

On the other hand, the amount of water absorbed by WF-mortar was higher than that of MS-mortar at all ages. The water absorption of MS-mortar and WF-mortar increased from 11.93% to 14.22% and 11.97% to 16.82% at 7 and 28 days, respectively. These findings indicate that despite the low water absorption of waste flint, the mortar prepared using it exhibited high water absorption. This could be explained by a high presence of interstice voids between particles of WF, suggesting that the amount of binder used was insufficient to fill these voids due to a lower fine content and the angular shape of coarse particles [14].

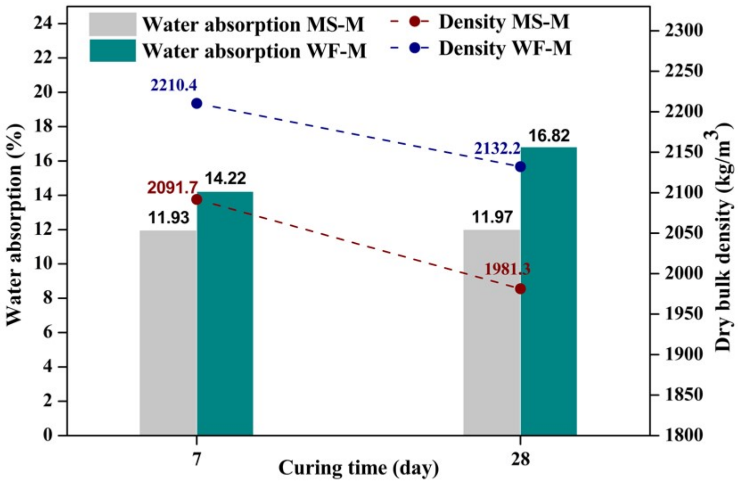

Figure 4. Dry bulk density and water absorption of MS-mortar and WF-mortar at 7 and 28 d.

3.2.2 Compressive strength and flexural strength

Figure 5 shows the effect of waste flint on the flexural strength of mortars after 7 and 28 days of curing. The results indicate a decrease in the flexural strength of the mortar with the total replacement of MS with WF, reducing from 4.85 MPa to 4.29 MPa and from 6.14 MPa to 6.03 MPa at 7 and 28 days, respectively. At 7 days, the flexural strength of WF-mortar was 23.31% lower and only 1.79% lower at 28 days compared to MS-mortar. This suggests that WF-mortar has nearly the same flexural strength as MS-mortar. Despite the lower flexural strength of WF-mortar at an early age, it significantly improves with time, which is due to the irregular shape of particles and strong adhesion between particles and the cement paste as reported in [16].

Three specimens were then subjected to compressive strength testing to figure out their average values. ***Figure 6*** presents the impact of WF on the average compressive strength of mortars cured for 7 and 28 days. Similar to flexural strength, compressive strength declined for all ages with the total replacement of MS with WF, reducing from 20.71 MPa to 15.17 MPa at 7 days and from 25.56 MPa to 19.01 MPa at 28 days. This decrease in compressive strength of WF-mortars correlates with a reduction in their dry bulk density and a growth in water absorption, caused by high percentage of voids in the WF-mortar matrix.

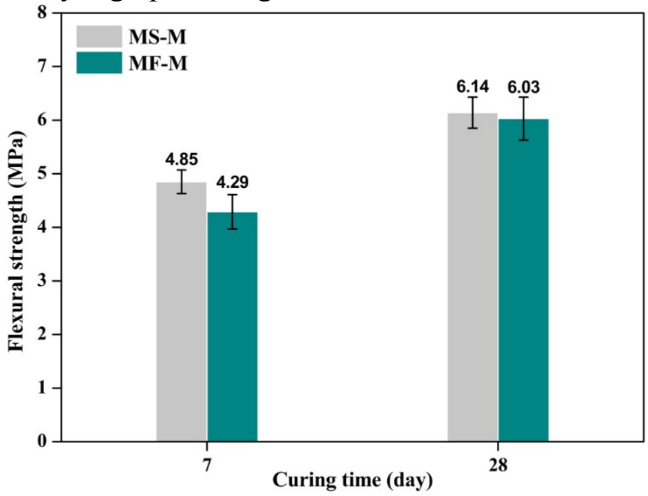

Figure 5. Flexural strength of MS-mortar and WF-mortar at 7 and 28 d.

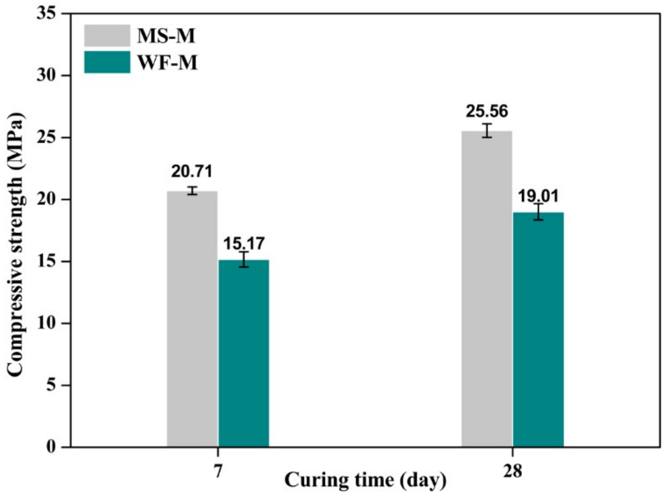

Figure 6. Compressive strength of MS-mortar and WF-mortar at 7 and 28 d.

3.2.3 XRD and microstructure analysis

The XRD analyses were conducted to evaluate the impact of replacing MS with WF on the formation of cement hydration products. ***Figure 7*** presents the XRD patterns of MS-mortar and WF-mortar after a 28-day curing period. Despite the selective removal of a part of the sand particles from the mortar matrix before analysis, both mortars retained the mineralogical composition of the original sand, with WF-mortar exhibiting the presence of quartz, dolomite, and fluorapatite, and MS-mortar containing quartz and albite. Both mortars exhibited the formation of primary hydration products, including portlandite, ettringite, and calcium silicate hydrates, which are essential components for high resistance. The presence of these phases in WF-mortar confirms that incorporating WF has no adverse effects on cement hydration. Additionally, the presence of calcite can be attributed to the carbonization reaction.
The Interfacial Transition Zone (ITZ) is a critical zone in mortar, significantly influencing its strength. After subjecting mortar specimens to flexural strength testing, the microstructure of fracture path into mortar specimens was analyzed. ***Figure 8*** provides a detailed view of the mortar microstructure after 28 days of testing for both WF-mortar and MS-mortar. In WF-mortar ***Figure 8*** (a), the fracture path passed through particles, indicating a robust ITZ between WF and cement paste. Conversely, ***Figure 8*** (b) shows fractures passing around particles along boundaries between MS-mortar, with particles being pulled off from their place, confirming a weaker ITZ. These distinctions can be attributed to the smooth surface and spherical shape of MS particles, providing an advantage over the rough surface and angular shape of WF particles [17]. These findings align with flexural strength results, demonstrating a significant improvement in WF-mortar flexural strength at later ages. Furthermore, the presence of large pores, resulting from insufficient binder to fill interstice voids due to the coarser property of sand, and small pores due to water evaporation.

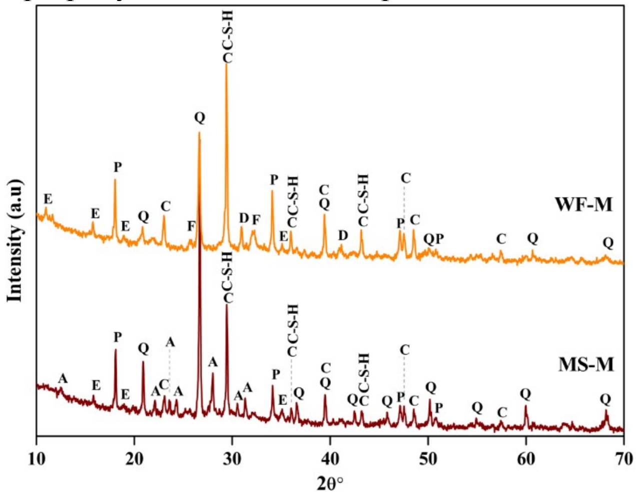

Figure 7. XRD patterns of MS-mortar and WF-mortar at 7 and 28 d.

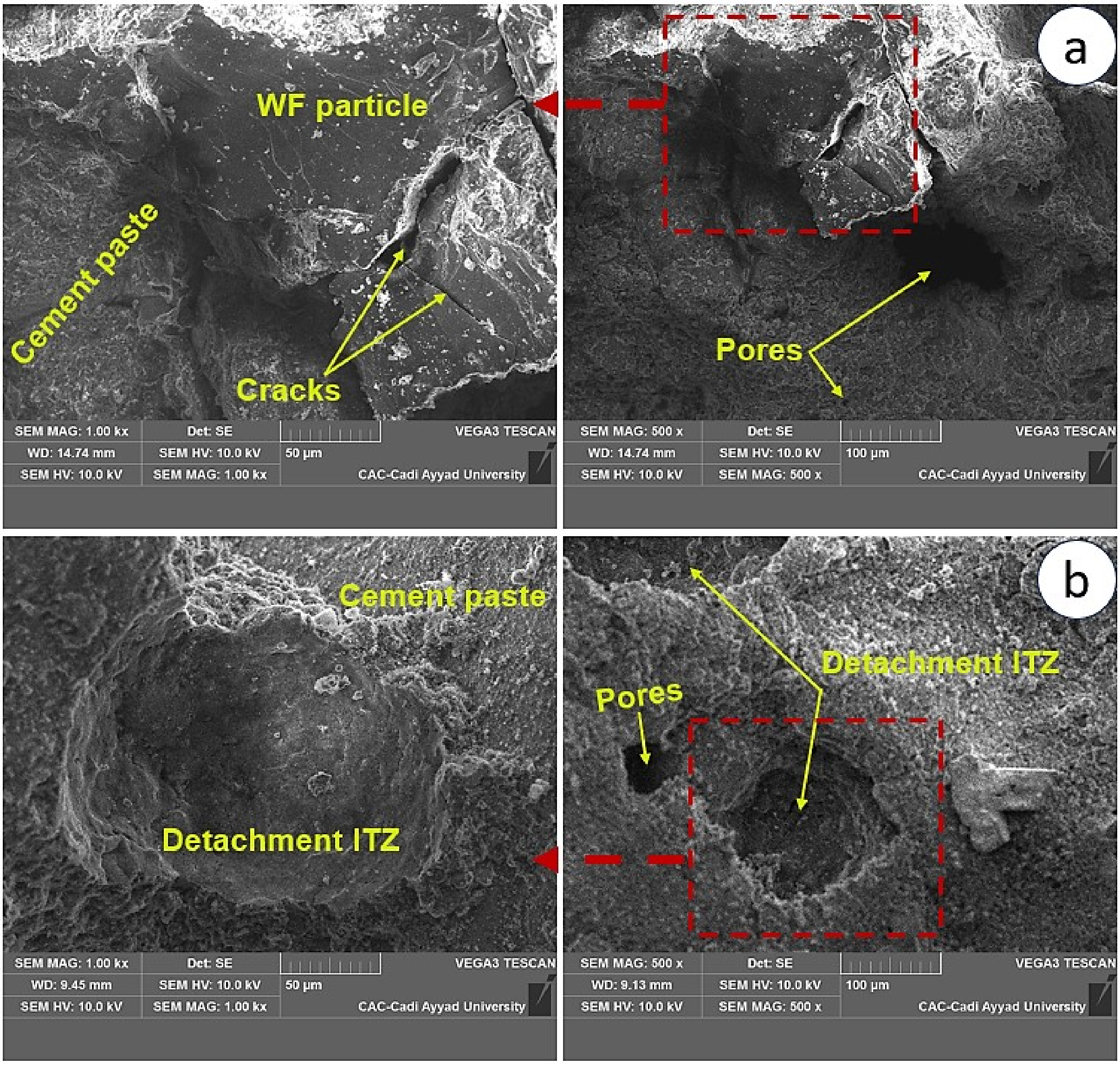

Figure 8. SEM images of ITZ between sand particles and cement paste. a) WF-mortar; b) MS-mortar.

4 CONCLUSIONS

This study successfully explored the potential of recycling WF from Moroccan phosphate interlayers as a fine aggregate for producing cement mortar. The main findings and conclusions are summarized as follows:

(1) The incorporation of WF results in a decrease in both compressive and flexural strength in cement mortar. However, a significant improvement is observed in the flexural strength of cement mortar with WF as the fine aggregate, reaching values comparable to MS-mortar at later ages.

(2) The ITZ between WF and cement paste exhibited greater compactness compared to the ITZ between MS and cement paste. The fracture path under the bending load traversed through the WF particles and extended around the boundaries of MS.

(3) Optimizing the replacement percentage of MS with WF could be a perfect suggestion to enhance the overall properties of cement mortar. By combining both sands, MS grains effectively fill the interstice voids between WF particles, leading to reduced water absorption in the mortars. Additionally, WF contributes to other beneficial properties, such as lowering the density of the mortars and establishing a robust Interfacial ITZ with the cement paste.

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