

Article

The Influence of the Magnesium-to-Phosphate Molar Ratio on Magnesium Potassium Phosphate Cement Properties Using Either Wollastonite or Volcanic Ash as Fillers

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Abstract: The use of the fillers wollastonite and volcanic ash for the formulation of magnesium phosphate cements prepared at magnesium-to-phosphate molar ratios of 2, 3 and 4 has been investigated, with the objective of evaluating these formulations for the encapsulation of aluminium radioactive waste. The workability, mechanical strength, dimensional stability, pH, chemical composition and mineralogical properties of cement pastes and mortars were examined. All cement pastes presented fast setting, and the workability was only good at 3 and 4 M. The cement mortars presented high compressive strength and dimensional stability. K-struvite was confirmed as the sole reaction product of the reaction for all formulations. The pH of the cement pastes, measured in suspensions, achieved values in the range of 7.8 to 9.5 after the first days of setting, exceeding pH 8.5 for the 2 and 3 M formulations. pH values below 8.5 are theoretically preferred to avoid potential aluminium corrosion. Both fillers presented adequate characteristics (good workability, chemical compatibility) to be used in the formulation of magnesium phosphate cements. The increasing magnesium-to-phosphate molar ratio prevented unwanted efflorescence and increased the mechanical stability of the cement.

Keywords: magnesium phosphate cement; radioactive waste; encapsulation; volcanic ash; wollastonite



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1. Introduction

Aluminium-containing radioactive waste is generated from nuclear fuel cladding materials and components of the fuel rods and other contaminated parts used in the reprocessing of nuclear fuels [1,2]. This waste, classified as low- and intermediate-level radioactive waste (LILW), must be carefully managed and conditioned in a stable matrix to be securely disposed for a long period of time [3].

Aluminium is a highly reactive metal that rapidly forms a protective oxide layer when exposed to air or water. This layer provides an excellent corrosion resistance that remains stable in a pH range between 4.5 and 8.5 [4]. Under alkaline conditions, the protective layer of aluminium (Al_2O_3) is corroded by hydroxides in a first stage and by water in a second stage, generating hydrogen gas that may produce internal pressures within the encapsulating matrix. Consequently, this could cause enough volume expansion to create internal fractures that could lead to the leakage of radioactive waste [5].

In recent years, magnesium phosphate cements (MPCs) have drawn a lot of interest for their ability to immobilize waste and, specifically, for the encapsulation of radioactive waste-containing reactive metals, such as uranium, aluminium fuel cladding and magnesium alloys [6–12]. MPCs are characterized by their short setting time, high compressive strength, resistance to chemical attack, low pH and low shrinkage [13–15].

MPCs are formed through an acid–base reaction between stoichiometric MgO and a soluble phosphate in the presence of water to produce struvite, or as specifically expressed in Equation (1), K-struvite [16].



Typical acid phosphates for MPC production are $(\text{NH}_4)_2\text{HPO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, KH_2PO_4 and NaH_2PO_4 ; however, monopotassium phosphate (KH_2PO_4) has three advantages over its analogues: (1) it reacts rapidly in contact with water, releasing a large amount of heat; (2) it is less soluble in water than ammonium or sodium salts, delaying the reaction of the cement and reducing the amount of heat released; and (3) it avoids noxious ammonium gas emissions during cement setting [16].

Depending on the MgO/ KH_2PO_4 (Mg/P) molar ratio and the water/cement (w/c) mass ratio (considering cement = MgO + KH_2PO_4), chemical reactions can form various expansive interphases prior to the formation of potassium struvite. At pH levels above 6.3, phosphorösslerite ($\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$) and a hydrated potassium magnesium phosphate ($\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$) are formed as intermediates. At pH levels below 6, newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) is formed as an intermediate phase [10].

Other studies show a complexity in the hydration of magnesium potassium phosphate cements (MKPCs) which is largely influenced by the w/c ratio [16]. Lahalle et al. [17,18] studied two MKPC formulations with a Mg/P molar ratio of one and two w/c mass ratios of one and 100. They observed that a w/c ratio of 100 resulted in the precipitation of the intermediate $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, followed by K-struvite and cattite ($\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$). The w/c ratio of 1 increased the presence of intermediates such as $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and phosphorösslerite. Xu et al. [16], using a Mg/P molar ratio of four and a w/c mass ratio of 10, obtained the same hydration intermediates and a late formation of K-struvite. When the Mg/P molar ratio is one and the w/c mass ratio is 0.2, newberyite is formed as an intermediate hydrate [19]. These authors also studied a Mg/P molar ratio of eight and two w/c mass ratios (0.5 and 5), and found that the w/c ratio = 0.5 avoided the presence of intermediate hydrates but produced a delay in the formation of potassium struvite and traces of brucite ($\text{Mg}(\text{OH})_2$).

A Mg/P molar ratio of one is favourable for obtaining K-struvite. However, an excess of MgO has also been shown to be beneficial. High Mg/P molar ratios (above four) are used for remediation purposes for damaged concrete [20], whereas Mg/P ratios below four are used for waste immobilization due to low pH values [16].

An excess of unreacted MgO at Mg/P molar ratios above four can lead to brucite formation and cement volume expansion. At low Mg/P ratios, efflorescence has been observed in addition to expansion [16].

The Mg/P molar ratio directly influences the hydration rate, setting time and mechanical strength [13]. Yang and Wu [20] found that high Mg/P ratios led to increased mechanical strength, concluding that Mg/P molar ratios of 4:1 and 5:1 were optimal. Other studies indicated that an excess of MgO accelerates the hydration reaction and reduces the setting time, but high levels of excess MgO can lead to high heat release and damage to the resulting product [13].

MKPCs are highly exothermic and generate a large release of heat, which accelerates the setting of the cement. The use of retarders, such as borax or boric acid, can slow the hydration kinetics and control the heat release [17,21]. Retarders are added in low proportions, typically below 3 wt.% [17], and their addition increases the setting time from a few minutes to several hours [22]. Furthermore, use of low-cost mineral additions that have no or a negligible contribution to the acid–base chemical reaction (fillers) such as fly ash, blast furnace slag, wollastonite, pumice or metakaolin [23–28], contributes to reducing the reactivity of MgO and decreasing production costs.

Wollastonite and volcanic ash are mineral materials of a different nature, availability and cost, but their study in MKPC formulations is necessary since fly ash, a by-product generated from coal-fired electricity generation, usually considered a reference filler mate-

rial for MKPC formulations [25,29,30], is now in decline [31], and less of this material will be generated with the foreseen closure of coal thermal power plants.

Wollastonite is an inosilicate mineral that shows low reactivity in Portland cement (PC) matrices, possibly due to the high pH of the pore solution (13–14), where wollastonite is more stable than C-S-H and does not react. At low pH levels, wollastonite is relatively soluble and releases calcium and silicate ions. Its presence in MKPC reduces heat generation and increases the mechanical strength [27].

Volcanic ash is considered a pozzolanic material in PC systems. Its pozzolanic properties depend on its chemical composition, reactive silica content, specific surface area, structural defects and degree of crystallinity. Preheating can increase the pozzolanic activity and improve the final strength by increasing the amount of reactive silica or amorphous phase [32]. The development of mechanical strength can vary depending on the size of the volcanic ash. The finer the ash, the higher the pozzolanic activity and strength [33].

Several studies carried out on PC systems with volcanic ash have shown that the presence of 0–30 wt.% volcanic ash causes a decrease in mechanical strength at early ages. On the other hand, with the increasing age, the strengths increased with higher volcanic ash contents [33]. In general, the presence of high levels of volcanic ash results in good workability, a high resistance to chloride penetration, high mechanical strength and good durability [34,35], despite the fact that these characteristics may not be displayed in MKPC systems due to the lack of chemical reactivity in the acid–base reaction. Volcanic ash has not been yet reported in the literature for being added as a filler in MPC formulations, but it has similar chemical and mineralogical characteristics to pumice, metakaolin, wollastonite, blast furnace slag or fly ash used in previous works (high content of Si, Al and Fe and a dominant silicate and silicoaluminate mineral composition).

The aim of the present work is twofold: (a) to evaluate the behaviour of two different fillers in the formulation of MKPC, wollastonite and volcanic ash, and (b) to study the effect on these MKPC formulations as a function of the Mg/P molar ratio, considering 2, 3 and 4 M, with implications for the encapsulation of radioactive aluminium waste. Most studies related to MKPC formulations for the encapsulation of radioactive waste assume only formulations with low Mg/P ratios to maintain pH conditions close to neutral and mitigate the potential Al corrosion. The present study explores the variability of characteristics using different fillers and increasing the Mg/P ratio. The formulations consider the minimum water content necessary to achieve good workability and produce K-struvite as the main reaction product, avoiding potential hydration in the long term with the residual MgO, which could produce brucite and generate expansion in the solid.

2. Materials and Methods

2.1. Raw Materials

High-purity, hard-burn MgO, calcined at temperatures ranging from 1000 to 1500 °C, was supplied by Martin Marietta Inc. with the commercial name of MAGCHEM 10CR. The KH_2PO_4 was provided by Seminsa, being a highly soluble salt, used as a fertilizer. Boric acid, with a purity of >99.5 wt.%, was used as the setting retarder.

The volcanic ash used in the present study was collected at the island of La Palma (Canary Islands, Spain). It was produced as a consequence of the volcanic eruption that took place from September to December 2021 at the Cumbre Vieja volcano. The eruption emitted more than 10 million cubic meters of ash and pyroclastic materials, the deposit of most of which covered large extensions of the island's surface. The BET specific surface area (SSA) of the raw material was $0.6 \pm 0.05 \text{ m}^2 \cdot \text{g}^{-1}$. The particle size distribution presented monomodal frequencies, with $D_{10} = 158 \text{ }\mu\text{m}$, $D_{50} = 444 \text{ }\mu\text{m}$ and $D_{90} = 844 \text{ }\mu\text{m}$ (D percentile values indicate the size below which 10%, 50% and 90% of all particles are found). The colour of the aggregates observed on sight was black, mostly influenced by the high content of iron. The morphology observed with an SEM (scanning electron microscope) revealed vitreous rounded aggregates (Figure 1). These aggregates were unevenly covered by iron deposits. Chemical punctual EDX (energy dispersive X-ray) analyses confirmed high

contents of silicon, aluminium and iron (over 20 at.% each), but also relevant contents of calcium, sodium, magnesium, potassium and titanium (in a range from 3 to 8 at.%). The mineralogy determined through XRD (X-ray diffraction) mainly showed the presence of ferromagnesian minerals presenting a low degree of crystallization (olivine, pyroxene, forsterite, augite, amphibole), with the addition of silica minerals (tridymite, cristobalite), mullite, plagioclases (anorthite, albite), Fe and Ti oxides (rutile, magnetite) and amorphous components.

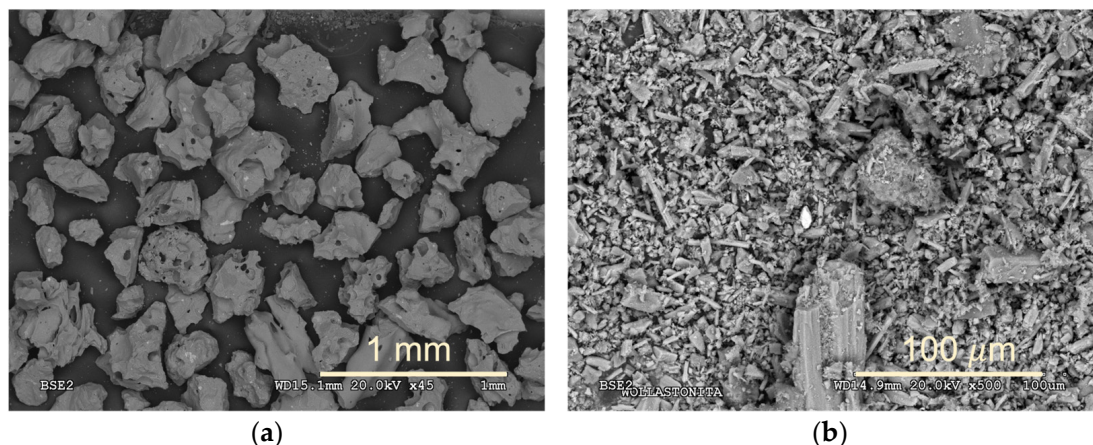


Figure 1. SEM images of (a) volcanic ash and (b) wollastonite.

The wollastonite was provided by Crimidesa. This raw mineral was extracted from the biggest wollastonite deposit in Europe, located in Aldea del Obispo (Salamanca, Spain). The BET SSA of wollastonite is $6.5 \pm 0.5 \text{ m}^2 \cdot \text{g}$. The particle size distribution showed a multi-modal frequency, with $D_{10} = 6.3 \text{ }\mu\text{m}$, $D_{50} = 41.3 \text{ }\mu\text{m}$ and $D_{90} = 216 \text{ }\mu\text{m}$ in the commercially milled presented form. The visual colour was greyish-white, and the morphology observed with the SEM manifested tabular aggregates of a much smaller size than the volcanic ash (Figure 1). The chemical composition determined through punctual EDX analyses corroborated that the dominant elements were silicon and calcium (38.5 and 48 at.%, respectively), while aluminium, magnesium, iron, potassium and sodium were all below 7 at.%. The mineralogy contained mainly wollastonite and parawollastonite with other accessory minerals, including quartz, K-feldspar, plagioclases, calcite, diopside, gypsum and anhydrite.

The chemical composition of MgO and both fillers, measured via X-ray fluorescence (XRF) is presented in Table 1.

Table 1. Chemical composition of MgO and the filler materials, expressed in wt.%.

Oxide	MgO	Volcanic Ash	Wollastonite
SiO ₂	0.5	35.33	41.21
Fe ₂ O ₃	0.3	18.81	3.68
CaO	1.9	13.53	43.31
Al ₂ O ₃	0.1	11.27	4.98
MgO	95.3	7.14	2.45
TiO ₂	-	4.88	0.54
Na ₂ O	-	4.87	1.26
K ₂ O	-	2.06	1.64
P ₂ O ₅	1.7	0.97	0.22
MnO	0.1	0.27	0.12
SrO	-	0.19	0.40
SO ₃	-	0.12	0.06
Σ others	-	0.58	0.14

2.2. Preparation of MKPC Mortars and Pastes

A filler (either volcanic ash or wollastonite), MgO, KH_2PO_4 , deionized water, H_3BO_3 and CEN standard sand according to EN 196-1 (only for the formulation of cement mortars) [36] were the materials used for the preparation of the MKPC pastes and mortars.

The MKPC pastes were prepared in two steps. First, the solid materials (MgO, KH_2PO_4 and filler), excluding boric acid, were mixed for 5 min with a mechanical stirrer. A parallel process was also performed for dissolving H_3BO_3 in water. Then, the liquid was added to the solid and mixed for 5 min. For the mortars, the solid mix also included normalized sand.

Two different water/cement ratios were used depending on the preparation of the pastes (0.3) or mortars (0.4). Since the addition of sand increased the total solid mass, the cement mortars needed more water than the pastes in order to ensure adequate workability. The water/solid ratio was, however, lower in the cement mortars than the pastes. The filler/cement mass ratio (considering cement = MgO + KH_2PO_4) decreased according to the increasing Mg/P molar ratio. Three cement paste and 3 cement mortar formulations were prepared according to the following Mg/P and filler/c molar and mass ratios, respectively: 2, 1.06; 3, 0.74; and 4, 0.5. The sand/c mass ratio = 1, for the mortars, and the H_3BO_3 /c mass ratio was 0.02 for both formulations, pastes and mortars. All samples were cured in sealed plastic bags in a curing chamber set at a fixed temperature of $20 \pm 1^\circ\text{C}$ for periods of 7, 28 and 90 days.

2.3. Methods

The SSA (BET-method) was determined through N_2 -adsorption with a Gemini V analyser from Micromeritics. The particle size distribution was determined with a Malvern Mastersize 3000 equipment (Malvern Panalytical, UK).

Mortars of $4 \times 4 \times 16 \text{ cm}^3$ were prepared to measure compressive strengths after 7, 28 and 90 days with a Matest Compression E161-03N tester (Matest, Italy) according to the European norm EN 196-1:2016 [36]. Also using those same prismatic dimensions, but using three gang moulds, the dimensional stability was measured in cement mortars using a Matest Length Comparator E077 (Matest, Italy) after 7, 28 and 90 days. Each presented value of compressive strength and length change was averaged from three individual samples.

The workability, setting time and chemical and mineralogical characterization were measured for the MKPC pastes. A mini-slump test was used to measure the workability in a cone with a 5.7 cm height and diameters of 1.9 cm at the top and 3.8 cm at the base. The slump area was calculated using the Image J software (v. 1.53), calibrated using a scale [37]. The setting time was tested using an automatic Vicat Needle Matest Vicatronic E044N (Matest, Italy) according to the ASTM-C191 norm [38].

The pastes were prepared for pH measurement at different ages (1, 2, 7, 15, 30, 90 and 180 days). At the end of each time point, the pastes were ground and suspended in deionized water with a water/solid (w/s) ratio of 1 [39] and stirred for 5 min. The pH was measured in the suspensions.

The pastes used for mineralogical characterization were immersed in isopropanol to stop hydration according to technical recommendations for further cement characterization [40]. XRD analyses were performed after 7, 28 and 90 days of curing on a Bruker D8 instrument (Bruker Corporation, Billerica, Massachusetts, USA) with a copper anode X-ray tube ($\lambda(\text{K}\alpha_1) = 1.54056 \text{ \AA}$), measured at a 2θ angle from 3° to 70° with a step size of 0.02° . The XRD diffractograms were analysed and semi-quantified using the X'PERT Highscore Plus software (v. 3.0.5) [41]. Firstly, the different phases present in the diffractograms were identified, and then quantification was performed through a Rietveld analysis, refining the following parameters: background, zero shift and sample displacement, as well as the scale factor, preferred orientation and unit cell of each of the phases present in the samples.

The SEM-EDX studies were carried out after 28 days with a JEOL JM-6400 microscope coupled to a LINK LZ_5 EDX analyser. The voltage used was 20 kV and the samples were coated with gold, with an average layer of 15 nm.

3. Results

3.1. Fresh Paste Properties: Workability and Setting Time

The results of the setting time and workability of the pastes are shown in Table 2. In general, MKPCs have faster setting time than PCs and, therefore, the development of mechanical strength is slower than for PCs [42]. Similar initial and final setting times were observed with volcanic ash for the formulations 2 M and 3 M, but when the Mg/P ratio was increased to 4 M, a slightly increased setting time was observed. In the case of wollastonite, the initial setting time was similar for 2 M and 4 M and shorter than for 3 M. The final setting time was also faster for 4 M, indicating a change in trend from 3 to 4 M. The results were in a similar range to previous studies evaluating different filler materials for MKPC formulations with Mg/P = 1–1.7 M [7,28].

Table 2. Setting time and workability of MKPCs using either volcanic ash (VA) or wollastonite (Wo).

Formulation	Initial Setting Time (h)		Final Setting Time (h)		Flow Area (cm ²)	
	VA	Wo	VA	Wo	VA	Wo
2 M	1.8	2.0	2.5	5.2	11.3	11.3
3 M	1.8	3.4	2.5	5.4	123.8	114.3
4 M	2.5	2.0	2.9	3.0	180.3	220.5

When the Mg/P molar ratio increases, the filler/cement ratio decreases, resulting in an increase in workability. Pastes prepared at 2 M presented poor workability, while at 3 and 4 M, the fluidity and workability of the pastes were excellent. Rather than the Mg/P molar ratio, this behaviour was related to the w/s mass ratio that increased from 0.15 (2 M) to 0.17 (3 M) and 0.20 (4 M). The w/s ratio used in the present formulations was much smaller than 0.35, typically used with PC in the UK nuclear industry [7].

None of the prepared formulations presented efflorescence, reported when either $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ or phosphorrrösslerite were detected [16,27], and often observed with MKPC formulations with lower Mg/P molar ratios.

3.2. Compressive Strength

Figure 2 shows the compressive strengths of mortars with Mg/P ratios of 2, 3 and 4 M with wollastonite and volcanic ash fillers after 7, 28 and 90 days of curing. In general, the compressive strength increased with the curing time. This increase was better appreciated in the samples with wollastonite, where the strength improved by 112% from 7 to 90 days for 2 M, 52% for 3 M and 77% for 4 M. In samples prepared with volcanic ash, the strength after 7 days was initially higher than with wollastonite, but the improvement with time up to 90 days was lower, 26% for 2 M, 18% for 3 M and 17% for 4 M.

Mechanical strength results determined for the MKPC samples using wollastonite, with a Mg/P molar ratio = 2.7 and variable w/s mass ratio (0.25 and 0.5), offered substantial differences after 28 and 90 days, with the formulation with a lower w/s ratio exhibiting around a seven-times-higher strength (70 MPa after 90 days). The authors observed that the addition of wollastonite increased the mechanical strength [27]. In comparison with the results obtained by Dieguez et al. [28], who used MKPC formulations with Mg/P = 1 and w/c in the range of 0.51–0.75, the compressive strength achieved in the present study was higher for all formulations, indicating the net effect obtained by increasing the Mg/P ratio and decreasing the w/c ratio.

In general, mechanical strength increases with hydration time, which may be related to the continuous formation of K-struvite, which precipitates with a more condensed structure and improves the development of mechanical strength.

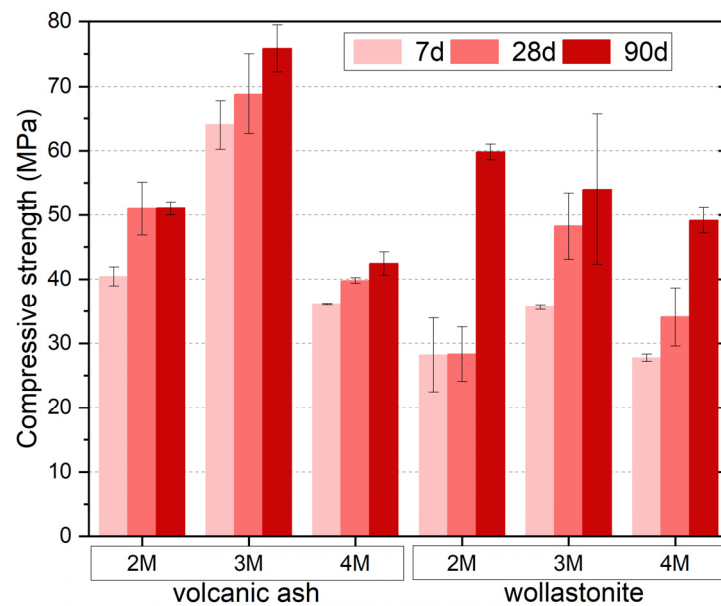


Figure 2. Compressive strength of MKPC mortars.

3.3. Dimensional Stability

The length change of the mortars was measured after 7, 28 and 90 days, and the results are shown in Figure 3. In general, the length changes were not much affected by either the Mg/P ratio or the curing time, after 7 days, for the formulations prepared with volcanic ash, but were highly variable for the formulations prepared with wollastonite. It was observed that the presence of wollastonite caused a shrinkage that increased with the hydration time, being higher for the Mg/P molar ratio of 4 M.

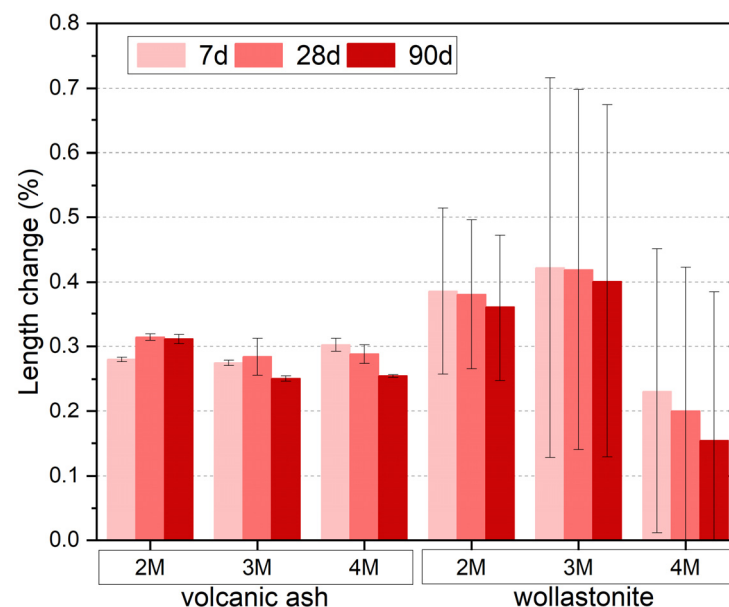


Figure 3. Length expansion of MKPC mortars.

This effect was also observed with the 4 M formulation with volcanic ash. For 3 M, an expansion of 0.28% was determined after 28 days, followed by a shrinkage of 0.25% after 90 days. For 2 M, there was an expansion of 0.31% after 28 days, which was similar after 90 days. Dieguez et al. [28] also obtained variations in dimensional stability in a similar range, using MKPC formulations with different fillers (fly ash, wollastonite, pumice and metakaolin), Mg/P = 1 and w/c ratios in the range of 0.51 to 0.75.

3.4. pH Evolution

Figure 4 shows the pH evolution over 90 days. The pH remained in a range between 7.5 and 9.5 for all the formulations except for the 3 M with wollastonite, which temporarily reached a pH = 10.5 after 15 days, and for the three formulations with volcanic ash, after 24 h, that were below pH 5.8, although the pH increased to over 7.8 after 48 h.

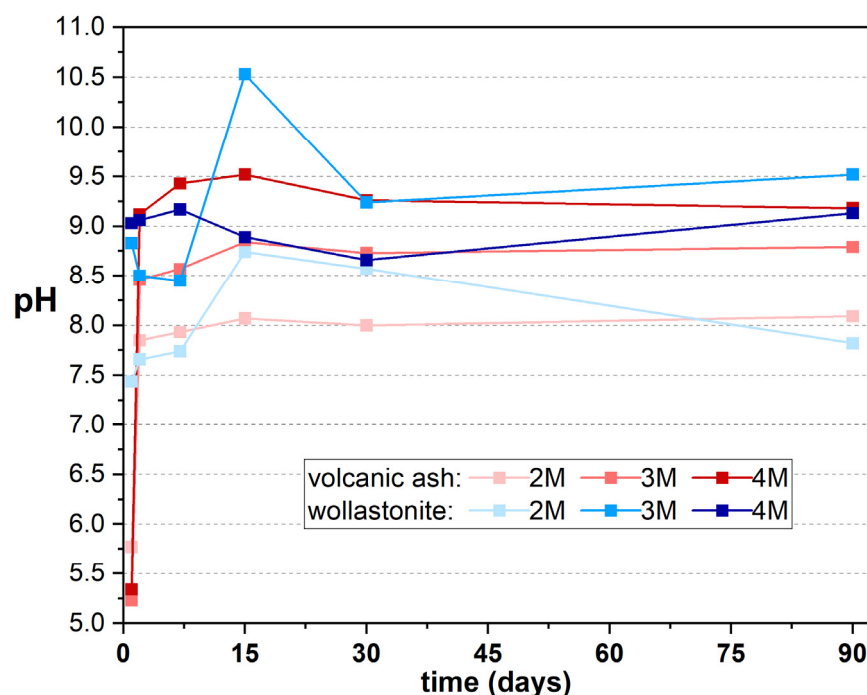


Figure 4. pH evolution of MKPC pastes' suspensions as a function of time.

Unfortunately, pH measurements were not performed in duplicate, and we cannot explain why the 3 M formulation with wollastonite presented such a pH increase within the time frame between 7 and 30 days. Except for that specific formulation after 15 days, the pH values increased with both the Mg/P ratio and the hydration time. Again, excluding that formulation, after a short pH stabilization period of 2–3 days, the pH remained in a narrow range. The pH variations from 7 to 90 days were lower than 0.25 units and all values were maintained in the range of 7.8 to 9.5.

3.5. Mineralogical and Microstructural Analysis

The XRD results for all the formulations, including both fillers and the three Mg/P ratios, are shown in Figure 5.

Independently of the formulation, the main reaction product observed in all diffractograms was K-struvite, whose reflection intensities increased with the curing time. Calcite was observed in all samples with wollastonite, with decreasing intensity with the increasing curing time. The rest of the minerals initially present in wollastonite and volcanic ash could also be observed in the MKPCs, although their XRD intensities were much lower compared to the large and sharp reflections of K-struvite and MgO.

With both fillers, unreacted periclase (MgO) was observed, while KH_2PO_4 could not be identified. The observation in detail of the reflections at $42.95\ 2\theta$ ($2.1\ \text{\AA}$) and $36.97\ 2\theta$ ($2.47\ \text{\AA}$), characteristic of periclase, indicated a decrease in intensity and area with the curing time, which is moderate from 7 to 28 days and minimum from 28 to 90 days. In addition, these reflections increased with the increasing Mg/P molar ratio, indicating the excess of unreacted MgO.

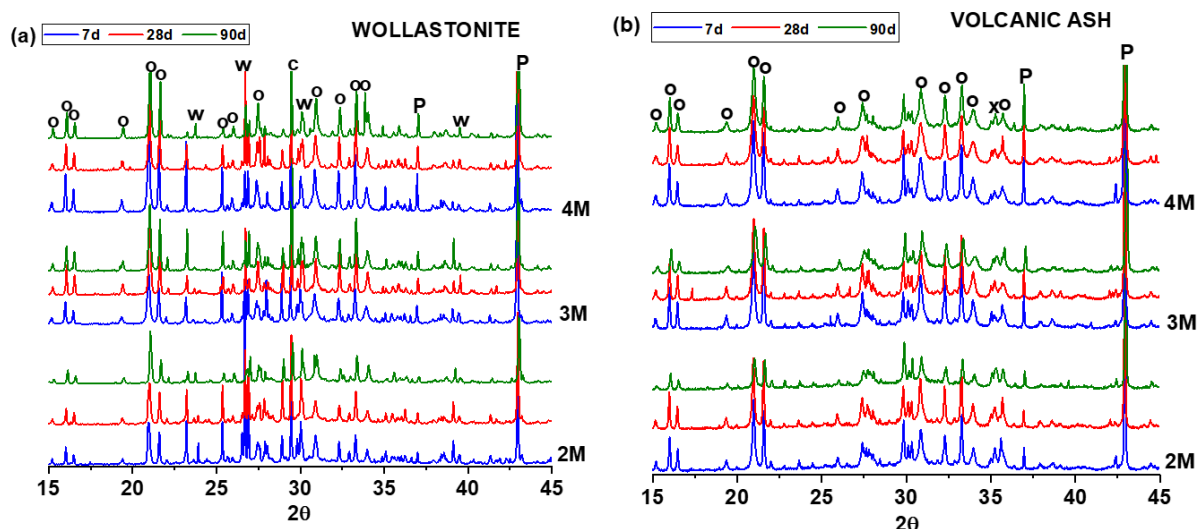


Figure 5. XRD patterns of MKPC pastes after 7, 28 and 90 days of curing. (a) Formulations with wollastonite; (b) formulations with volcanic ash. Legend: o: K-struvite (PDF file: 01-075-1076); x: mullite (PDF file: 01-083-1881); w: wollastonite (PDF file: 01-075-1396); c: calcite (PDF file: 01-083-0578); P: MgO (PDF file: 01-087-0651).

The reflection at $20.96^\circ 2\theta$ ($4.235 \text{ \AA}$), which corresponds with the family of planes {111} for K-struvite and it is the reflection of highest intensity, showed an increase in intensity from 7 to 90 days for the formulations prepared with wollastonite at 2 and 3M, but a decrease in all other formulations. Additionally, a slight shift to higher angles was observed for most of the formulations.

The semi-quantitative analyses performed using Rietveld refinement indicated an increase in both minerals, K-struvite and periclase, with the increasing Mg/P ratio, independently of the filler used. Thus, the K-struvite formed after 90 days for the Mg/P molar ratios of 2, 3 and 4 M represented 57, 60 and 65 wt.% with wollastonite, and 47, 58 and 65 wt.% with volcanic ash. The excess of periclase was semi-quantified within the range of 11–14 wt.% at 2 M, 14–18 wt.% at 3 M and 18–22 wt.% at 4 M, considering the formulations with both fillers and including the three curing times.

The SEM-EDX analysis was limited to studying the morphology and compositions of the mineral phases present in the cement paste samples cured for 28 days. The results are shown in Figures 6–8.

The main reaction product was K-struvite. As the analyses were performed on polished sections, the morphology of the K-struvite crystals was better observed when they were grown in cavities. K-struvite was identified as a tabular crystal growing in pores, whereas when growing in confined areas, its morphology presented more irregular crystals, in agreement with previous studies [25,29].

The formation of large struvite crystals in different pores was generally observed for both fillers (Figures 6 and 7). In general, as the Mg/P ratio increased, the size of the crystals increased and the faces became better defined. At 2 M, the formulations with wollastonite presented incipient crystal growth (Figure 6a), although the crystal habit could not be well differentiated. Prismatic crystals were better defined at 3 M (Figure 6b) and the size was increased at 4 M (Figure 6c). The EDX colour map presented in Figure 6d (3 M formulation), indicated a large, predominant K-struvite composition in the analysed surface, although several zones showed an excess of Mg (pink and purple colours) and silicate minerals coexisting in the matrix (orange colours).

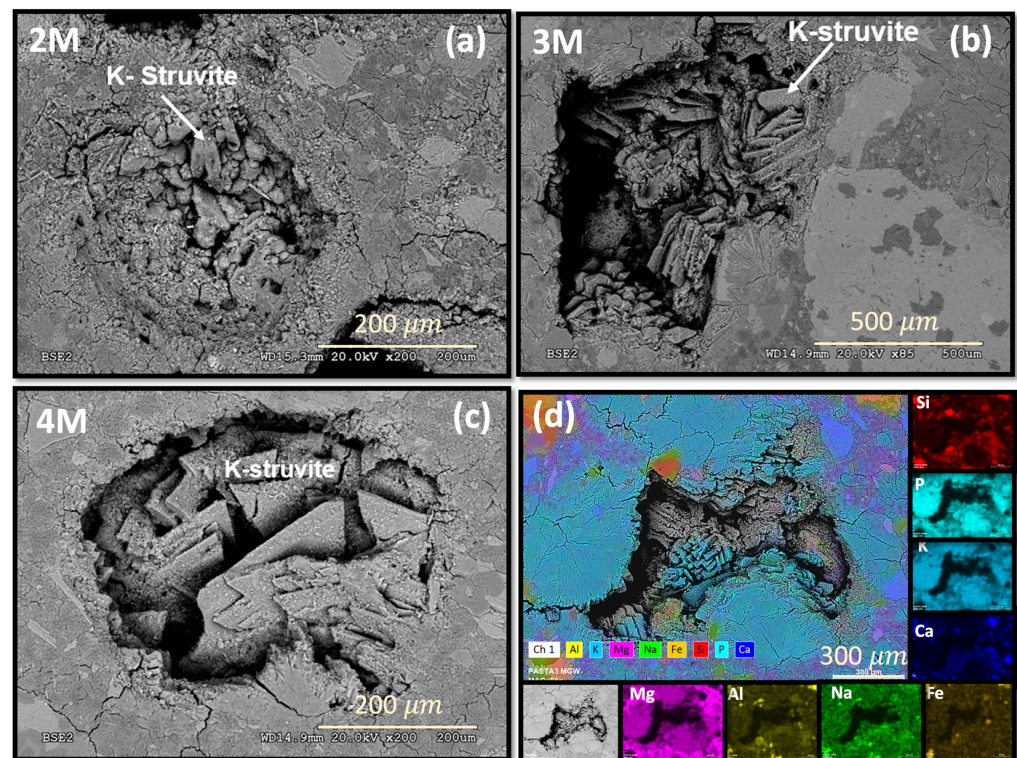


Figure 6. SEM images of MKPC pastes prepared with wollastonite at Mg/P molar ratios of (a) 2 M, (b) 3 M and (c) 4 M; (d) 3 M, colour map.

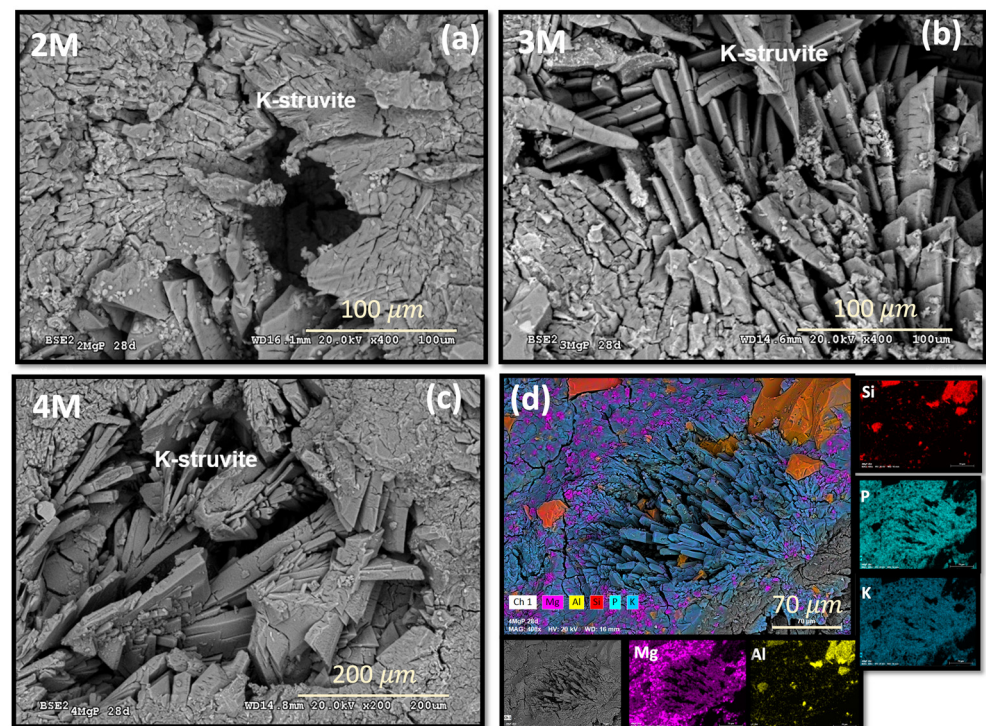


Figure 7. SEM images of MKPC pastes prepared with volcanic ash at Mg/P molar ratios of (a) 2 M, (b) 3 M and (c) 4 M; (d) 3 M, colour map.

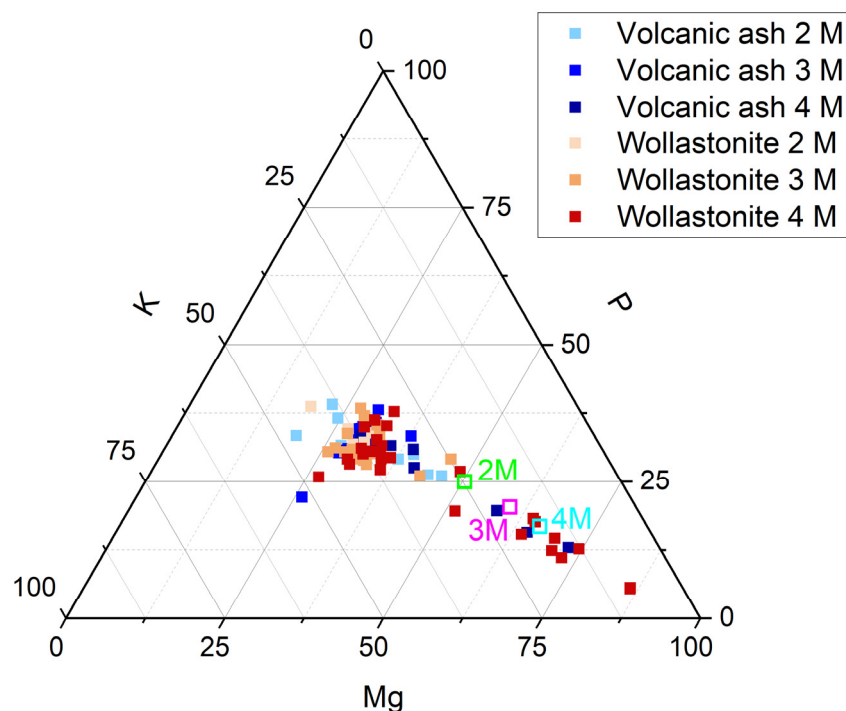


Figure 8. Percentages of Mg, K and P in MKPC pastes after 28 days' curing, measured via semi-quantitative EDX analyses. Atom ratios for theoretical formulations 2, 3 and 4 M are provided as a reference.

The MKPC formulations including volcanic ash presented K-struvite crystals with irregular tabular morphologies at the three Mg/P molar ratios, although the crystal sizes were not much larger at higher Mg/P ratios (Figure 7a–c). The colour maps also confirmed that K-struvite was the predominant phase formed in the formulations with volcanic ash, although coexisting with accessory minerals initially present in the filler, mostly silicates and silicoaluminates (identified by the orange colour in Figure 7d). An excess of MgO was observed (pink colour), becoming more evident with the increasing Mg/P ratio used in the formulations.

Numerous EDX analyses were performed on single small spots on the surface of differentiated aggregates and polished surfaces identifying different mineral grains, in samples cured for 28 days, considering all the formulations. The chemical atom ratios (%) of Mg, K and P are presented in Figure 8 in a ternary plot. Carbon and oxygen were excluded from each analysis and the atomic ratios were recalculated up to 100%. Other elements (mostly Si, Al, Ca, Fe and Na, but additionally, minor quantities of Ti, Mn, S, Cl, Zr and Zn) were not excluded. The data presented in Figure 8 (133 analyses) only account for those analyses presenting a sum of Mg + K + P > 90%. This considers some potential interference of the elements forming the surrounding minerals, mixed with the MKPC matrix or potentially included in the K-struvite composition, and could slightly affect the atom ratios, as the total sum of these three elements might be below 100%. Nonetheless, the interference is minimal, since the sum of Mg + K + P $\geq$ 99% for 65% of these analyses and is $\geq$ 95% for 92% of them.

Independently of the Mg/P molar ratio and the filler used in the formulations, the data indicated that the atomic ratio of Mg/K/P found in most of the compositions was near the stoichiometric 1:1:1 molar ratio, characteristic of K-struvite. Some dispersion of the data towards high Mg ratios and, consequently, low K and P ratios, was observed with the increasing Mg/P molar ratio, mostly attributed to an excess of unreacted MgO, as previously observed in the colour maps (Figures 6d and 7d).

Other EDX chemical analyses, discarded in Figure 8, clearly identified minerals initially present in the fillers' mineral assemblage: wollastonite, calcite, plagioclases, periclase and

Fe oxides in those formulations prepared with wollastonite, and Mg, Fe aluminosilicates, Fe oxides, plagioclases and periclase in the formulations prepared with volcanic ash.

4. Discussion

The acid–base reaction does not stop after the final set. It may be inferred that the hydration reaction does not complete after 90 days, as it seems that the strength continues to increase with the curing time and does not yet reach a plateau. However, the early strength achieved after only seven days for any the formulations studied was higher than 25 MPa and increased to values in the range of 42.4–75.8 MPa after 90 days, which is acceptable for radioactive waste immobilization. Mechanical strength has been related by several authors to be influenced by the w/s ratio, observing greater strength with lower w/s ratios, since the void space may be reduced, creating a denser cement matrix [9]. However, this relationship only fits with our results for the formulations prepared with wollastonite, considering the strength achieved after 90 days, as the w/s ratio in the cement mortars increased with the increase in the Mg/P ratio: 0.13, 0.15 and 0.16 for 2, 3 and 4 M.

Although all mortar formulations contained an excess of MgO that would not react to form K-struvite, the water/P molar ratio increased with the increasing Mg/P ratio: 4.8, 5.7 and 6.6 for 2, 3 and 4 M; therefore, water and KH_2PO_4 were the limiting components in the reaction. The 2 M formulation presented insufficient water to form stoichiometric K-struvite (5 mols of water per mol of phosphate are required to form K-struvite according to Equation (1)), but the 3 and 4 M formulations presented an excess of water, which might be justified since the mixing of materials of different grain sizes will not produce perfect homogenisation and will demand some extra water.

Several authors related the strengthening to the formation of K-struvite, which occurs during the first days of the acid–base chemical reaction [7,43] and develops, thereafter, slowly with the associated consumption of remaining MgO. No other crystalline mineral phases other than K-struvite were observed, neither in the present study nor in previous works [7,28]. Additional magnesium phosphate phases, such as phosphorösslerite or cattite, considered reaction intermediates, were only detected in other studies at high w/s ratios [17,18]. The strength development becomes significant when the free pore space is reduced, a relatively high packing density is attained and the particles bind themselves. The short compressive strength observed for the formulation with volcanic ash and Mg/P = 4, compared to 2 and 3 M, might be related to the fast set and the short difference in time from the initial to the final setting.

The type of water adsorption exerted to generate K-struvite and, subsequently, the MKPC characteristics, must have been influenced by the differences in the particle size distribution of wollastonite and volcanic ash. The volcanic ash exhibited uniform, spherical, large-size particles, but the wollastonite displayed smaller aggregates with a larger size distribution. Based on the analysis of the compressive strength data, it can be inferred that volcanic ash generated large pores where water was firstly accumulated and quickly consumed. As a result, the initial strength achieved was high but did not significantly increase with the curing time. Conversely, wollastonite would produce free water to be consumed faster from the larger pores, while free water located at micropores would be consumed more slowly, leading to larger increments of strength with the curing time. This slower evolving reaction might also be the cause that generated large errors in the length changes observed in the samples with wollastonite. Although the length changes were not large (0.15–0.4%), the reproducibility between samples was poor, and that might be related to the complex net of connected pores.

Thermodynamic calculations performed by other authors predicted the formation of magnesium calcium silicate hydrates (M-C-S-H) and hydroxyapatite. M-S-H and poorly crystalline hydroxyapatite were experimentally confirmed whilst studying the mineralogical evolution of MKPC systems using wollastonite [27], indicating a certain contribution of mineral addition to the cement hydrates assemblage, which is initially considered a filler material with no or negligible action in the acid–base reaction. A detailed structural study

has not been performed in the present study to confirm the mineral contribution of volcanic ash and wollastonite, and no evidence was found through XRD.

pH values below six were determined for the paste suspensions in the formulations prepared with volcanic ash after 1 day. In those pH conditions, newberyite could have formed as a reaction intermediate [19]. De Campos et al. [10] observed a minor presence of this mineral after 7 days in MKPC through XRD, but it was not detected in the present study. Thermodynamic data predict that K-struvite forms faster than any other phosphate hydrates and is able to replace newberyite at pH values above 8 [44]. At pH values above 10.5, brucite occurs. For aluminium metal encapsulation, a pH value in the range of 8–8.5, ensuring the stabilization of K-struvite that provides chemical and mechanical stability and maintaining electrochemical conditions for $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ passivation [45], would be ideal. Only the 2 M formulations maintain those pH conditions in the long term (>30 days), but since the electrochemical behaviour includes complex processes that do not only depend on pH, an evaluation of the interaction between Al metal and MKPC prepared at higher Mg/P molar ratios than two should be performed to either consider or discard those formulations.

5. Conclusions

MKPC formulations blended with either wollastonite or volcanic ash as filler materials and Mg/P molar ratios of two, three and four were prepared and characterized. The rheological, mechanical and mineralogical properties studied showed potential for the encapsulation of radioactive aluminium metal, although the curing time of this study was limited to 90 days and longer studies should be performed to ensure long-term performance. The increasing Mg/P molar ratio produced an increase in the pH. Cement pastes were prepared at 2 M and stabilized at a pH value near 8, below 8.5, which is thermodynamically considered the maximum pH where aluminium remains passivated. Formulations at higher Mg/P ratios should be, in principle, discarded, although electrochemical studies and experiments devoted to the chemical interaction between aluminium and MKPC should verify whether MKPCs prepared at 3 and 4 M, that produce pH values in the range of 8.7 to 9.5, are capable of generating corrosion.

The sole reaction product identified as a result of the acid–base chemical reaction was K-struvite, independently of the Mg/P ratio used in the study. Nevertheless, an excess of unreacted periclase was observed in all formulations, increasing its presence with the increasing Mg/P ratio. No intermediate reaction products were observed via XRD or SEM, although they have been normally detected in the short term and in systems with much higher water/solid ratios.

Further investigations should be performed to evaluate the durability of MKPCs under relevant conditions for aluminium encapsulation, including the homogeneity of the waste form and its leaching behaviour.

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