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Innovative application for bauxite residue: red mud-based inorganic polymer spheres as pH regulators

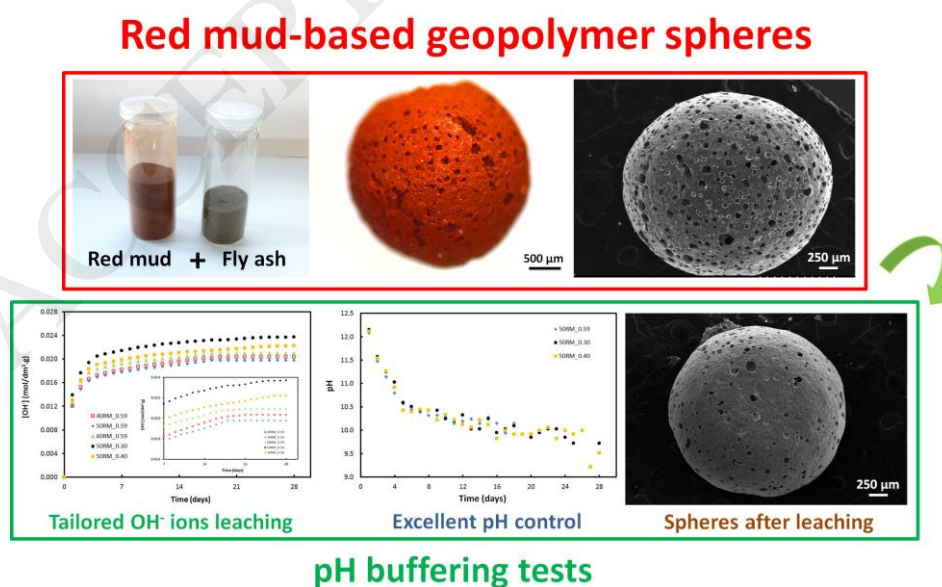
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Graphical Abstract:



Highlights

- Red mud-based geopolymer spheres (2.5 mm) were synthesised for the first time.
- The aluminosilicate sources of the geopolymer spheres were 100% waste-based.
- The spheres pH buffering ability in aqueous medium was evaluated.
- High OH⁻ leaching (0.0237 mol/dm³g) and narrow pH drop (2.4 pH units) was attained.
- This innovative recycling strategy may significantly reduce red mud disposal.

Abstract

In this study, and for the first time, red mud (RM)-based geopolymer spheres were synthesised, with varying porosity and RM content, and then their use as pH regulators was evaluated. The aluminosilicate sources of these inorganic polymers were 100 % waste-based, consisting of a mixture of RM and fly ash wastes. Geopolymer spheres containing up to 60 wt.% RM were successfully produced, while higher RM contents distorted the specimens' spherical shape. Results showed that alkalis leaching from the spheres over time can be controlled by their porosity, while the RM content induces only minor changes to leaching. The RM-based spheres leached up to 0.0237 mol/dm³g of OH⁻ ions from their structure, this being among the highest values ever reported for geopolymers. This allowed a continuous and prolonged pH buffer capacity with narrow pH decay over the 28 days (2.4 pH units), suggesting the use of the RM-based spheres as pH buffering materials in wastewater treatment and anaerobic digestion systems.

Keywords: bauxite residue; biomass fly ash; geopolymer; pH buffer capacity; alkalis leaching.

1. Introduction

Bauxite residue, also known as red mud (RM), is a by-product produced in massive quantities during alumina production by the Bayer process. Recent data shows that 115 Mt of alumina were produced worldwide in 2016 [1]. Considering that for each ton of alumina extracted from the ores around 0.8-1.5 t of RM [2] are generated, RM production would have equalled an impressive 92-172 Mt in 2016. Moreover, considering an annual production of ~ 120 Mt [3] the RM accumulated stockpile, estimated to be 3.5 Gt in 2014 [4], reached a distressing ~ 3.9 Gt in 2017. RM is a highly alkaline and toxic waste, which makes its recycling extremely challenging. RM is currently mostly disposed in large lagoons in slurry form, or in tailings dams as dry RM [5], which is very costly and raises serious environmental concerns. Fatal and environmentally catastrophic accidents involving RM storage, such as those that occurred in Ajka (Hungary) in October 2010 and Luoyang (China) in August 2016 [6], have raised public fears regarding RM management methodologies. These accidents demonstrate the urgency to find new management strategies for RM. One exciting approach could be the reuse of RM in high added-value applications, changing the paradigm to consider RM as a valuable resource, rather than being regarded as a waste. Numerous investigations have been performed aiming to develop viable recycling solutions for RM, namely as colouring agents for ceramic glazes [7], as amendments to immobilise contaminants in soil [5], as heavy metal [8] and dye adsorbents [9], and as raw materials in mortars [10] and cements [11]. Despite this, RM continues to be an unexplored waste material, mostly because its maximum incorporation content in large

scale applications (e.g. cements) is restricted by the RM composition (e.g. high sodium content) [12]. For these reasons, new possible solutions must be eagerly pursued to reduce the colossal RM stockpile. One interesting approach that may significantly reduce RM disposal is its alkaline activation to produce inorganic polymers, or geopolymers [13]. The interest in this technology is growing rapidly, as demonstrated by the sharp increase in the number of investigations over recent years (see Fig. 1). Geopolymers are mainly envisioned for structural applications [14], yet they present other exciting properties (e.g. alkalis leaching) that have been rather neglected. After geopolymerisation, free alkalis remain in the geopolymer structure, which are available for leaching, suggesting the possibility of using them as pH buffering materials. Nevertheless, the number of investigations addressing this feature is limited. Recently, the use of metakaolin-based geopolymer monoliths [15] and biomass fly ash (FA) spheres [16] as pH regulators was studied by the authors. These investigations demonstrated that the alkalis leaching may be controlled by the porosity, chemical composition of the raw materials, and by the solid-to-liquid ratio of the mixture [15, 16]. Other influential factors have also been investigated, in particular the nature [17] and concentration [18] of the alkaline activator, and the alkaline material particle size [19]. These important findings may be transferred to RM-based geopolymers. Studies considering the pH buffer capacity of RM containing geopolymers are rare, the exception being the work of Ascensão *et al.* [12] that produced porous RM-containing geopolymers by using aluminium powder as a foaming agent. The authors observed a narrow pH decrease (1.64 pH units) over 28 days when immersing cubic specimens (8 mm³) in distilled water. Despite these promising results, Ascensão *et al.* [12] used, in their best performing composition, a huge amount of alkaline activators (50.81 wt.%) and metakaolin (22.00 wt.%) which increase both the carbon footprint and production

cost of such geopolymers. Here, an innovative and more eco-friendly strategy was implemented, in which RM and biomass FA wastes were used (as alumina and silica sources) to produce 100 % waste-based geopolymer spheres (regarding the aluminosilicate source). This is the first ever investigation reporting the production of RM-based geopolymer spheres, and their subsequent use as pH buffering materials. These RM-based geopolymer spheres are expected to show much higher surface area than the previously reported RM-containing geopolymer monoliths [12] and, therefore, much higher pH buffering capacity. Moreover, in the present investigation, a lower amount of alkaline activators (38.31 wt.%) was used in comparison with previous studies, 50.81 wt.% [12], 43.79 wt.% [15] and 56.00 wt.% [16], which is beneficial both from an economic and environmental view point. The influence of RM content, and the use of non-aluminium-based pore forming agents, on the spheres' pH buffering capacity was evaluated by immersing the spheres in an aqueous medium.

This investigation intends to act as a proof-of-concept, demonstrating the feasibility of using high amounts of RM to produce 100 % waste-based (aluminosilicate sources) geopolymer spheres, which were then evaluated as pH regulators. The latter is of crucial importance, and may allow their use in wastewater treatment systems and in anaerobic digesters, where a strict pH control is crucial to enhance systems efficiency [20]. Hence, this is an innovative recycling strategy that may significantly reduce the disposal of RM that, despite the efforts over past decades, remains as an unexplored and hazardous waste material. This study explores the high alkalinity of red mud, which hinders its incorporation in common concrete, to produce an innovative and high added-value material that may be used in anaerobic digestion systems.

2. Experimental Conditions

2.1. Materials

Two wastes were used as geopolymerisation precursors: RM and biomass FA. RM was supplied by Alcoa (Spain), while FA was supplied by a Portuguese pulp and paper industry. Prior to mixing, RM was dried, milled and sieved, and then only particles below 75 μm were used. The FA was sieved and only particles below 63 μm were used. For the alkaline activation, a mixture of sodium silicate solution ($\text{SiO}_2/\text{Na}_2\text{O} = 3.09$; Chem-Lab, Belgium) and sodium hydroxide (ACS reagent, 97 %; Sigma Aldrich) was used.

Sodium dodecyl sulfate was used as a pore forming agent, while polyethylene glycol (PEG-600) was used to promote fast curing of the geopolymer spheres. Both reagents were supplied by Sigma Aldrich.

2.2. Geopolymers preparation

The geopolymer spheres were produced by using a suspension-solidification approach described elsewhere [16]. Five compositions were prepared, to evaluate the influence of RM and pore forming agent content on the spheres' leaching ability. Details of the mixture compositions are presented in Table 1. This experimental design allows the evaluation of two very important parameters affecting the geopolymers' leaching ability: i) the raw materials chemical composition, by using various RM:FA ratios; and ii) the geopolymers' porosity. Future work will address the influence of the activators nature and concentration on the geopolymers' OH^- leaching. As shown in Table 1, the blowing agent amount in the compositions varied between 0.30 and 0.59 g. These values were selected considering the dual effect of the foaming agent, which is known to enable the formation of spherical shapes, yet negatively affecting the

geopolymerisation at high incorporation levels [21]. Therefore, the maximum value used was set at 0.59 g, considering previous works by the authors [16, 22], while the lowest amount was set to ensure that the spheres floated after injection into the PEG medium.

The alkaline activator was mixed with water, RM and FA (amounts depending on the composition) in a planetary mixer for 2 min. Afterwards, the pore forming agent was added to foam the geopolymer slurry and the slurry mixed for another 5 min. Then, the slurry was injected into the PEG medium (under a bath temperature of 85 ± 5 °C) to produce the RM-containing spheres. Finally, the spheres were collected and cured for 7 days: for the 1st day at 40 °C and 65 % relative humidity, and the following days at ambient conditions.

2.3. Materials characterisation and analysis

The mineralogical compositions of RM, FA and the geopolymer spheres were evaluated by X-ray powder diffraction (XRD). The XRD was conducted on a Rigaku Geigerflex D/max-Series instrument (Cu K α radiation, 10–80 °, 0.02 ° 2 θ step-scan and 10 s/step), and phase identification by PANalytical X'Pert HighScore Plus software.

X-ray fluorescence (XRF, Philips X'Pert PRO MPD spectrometer) was used to determine the precursor's chemical composition.

Scanning electron microscopy (SEM - Hitachi S4100 equipped with energy dispersion spectroscopy, EDS – Rontec) was used for evaluating the geopolymer spheres' microstructure, while optical analysis (Leica EZ4HD microscope) was selected for the morphology analysis. EDS maps of the precursors were obtained using SEM (Hitachi SU-70).

To evaluate the suitability of the spheres to act as pH regulators, their OH^- leaching in water medium was measured following a previously reported leaching procedure [12, 15, 16]. For this purpose, 1 g of geopolymer spheres (cured for 7 days) was immersed in 60 mL of distilled water for 24 h. After 24 h, the spheres were moved to a new water bath and the process repeated until reaching 28 days immersion. Two samples per composition were tested.

The OH^- leaching rate was measured on a daily basis for all compositions by acid-base titration, using HCl solution as titrant and phenolphthalein as acid-base indicator. The pH of the medium was calculated using the predetermined concentration of OH^- [15].

The possible leaching of iron, chromium and lead from the specimens during their immersion in water was evaluated by atomic absorption spectroscopy (Avanta PV, GBC). These elements were selected considering the red mud chemical composition determined by XRF. Leaching was evaluated after 1, 2, 3, 21 and 28 days immersion of the geopolymer spheres which had shown the best pH buffering performance (see *section 3.2*).

3. Results and discussion

3.1. Precursors characterisation

The chemical composition of RM and FA, presented in Table 2, shows that RM is mainly composed of Fe_2O_3 , followed by Al_2O_3 , TiO_2 and SiO_2 , while the most abundant components of the FA are SiO_2 , CaO and Al_2O_3 . RM presents ~ 5 wt.% alkali metal oxides (Na_2O and K_2O), while the FA has an even greater content (~ 7 wt.%). These results, extracted from the raw materials chemical composition (see Table 2), are supported by the EDS elemental mapping shown in Fig. 2.

The XRD pattern of RM (see Fig. 3) shows the presence of numerous crystalline phases, hematite (Fe_2O_3) being the most abundant one. Additionally, small amounts of gibbsite ($\text{Al}(\text{OH})_3$), quartz (SiO_2), boehmite ($\text{AlO}(\text{OH})$), chantalite ($\text{CaAl}_2\text{SiO}_4(\text{OH})_4$), anatase ($\beta\text{-TiO}_2$), rutile ($\alpha\text{-TiO}_2$) and $\text{Na}_5\text{Al}_3\text{CSiO}_{15}$ were also detected. The FA show very intense crystalline phases in their XRD pattern, yet their composition presents lower complexity than that observed for RM, with quartz, illite ($(\text{K},\text{H}_{30})\text{Al}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_{2.x}\text{H}_2\text{O}$) and calcite (CaCO_3) being the observed crystalline phases. The crystalline phases of both precursors are in line with the components detected by XRF.

3.2. Inorganic polymer spheres characterisation

Typical photographs of the geopolymer spheres containing varying RM content are presented in Fig. 4, while photographs of geopolymer spheres produced with 50 wt.% RM and varying pore forming agent content are shown in Fig. 5. The images clearly demonstrate the feasibility of preparing geopolymer spheres with high RM content (up to 60 wt.%). It should be highlighted that this is the first time RM-based geopolymer spheres were successfully synthesised. The latter is of crucial importance, and could significantly mitigate this need for this waste's disposal. Previous studies have shown that geopolymer spheres produced using other raw materials (e.g. metakaolin, FA) present interesting potential for applications such as heavy metals adsorption [21] and pH buffering in anaerobic digesters [22], and for that reason, it is plausible to assume that these RM-based spheres may also be used in similar applications. The possibility of using the RM-based geopolymer spheres as a dye or heavy metal adsorbent will be considered in future work.

Fig. 4 shows a narrow size distribution for all compositions, with the diameter of the spheres being roughly 2.5 mm. Preliminary tests showed that the RM content affected the sphericity of the sample: for RM contents higher than 60 wt.%, the spherical shape was not maintained after injection of the geopolymer slurry into the PEG medium. In fact, in these preliminary tests the use of 70 wt.% RM and various foaming agent contents (0.0, 0.30 and 0.59) were evaluated. However, the compositions containing 0.30 and 0.59 g of foaming agent did not preserve their spherical shape, while those prepared without foaming agent did not float in the PEG medium, due to their higher density. For these reasons, the maximum RM content used was 60 wt.%. Nevertheless, the use of higher RM content may be feasible by modifying the PEG density or the injection medium. This possibility will be addressed in future work.

Fig. 5 illustrates the expected rise in porosity when increasing the pore forming agent amount, with higher porosity being particularly visible for the composition containing 0.59 g of pore forming agent. This is expected to affect the geopolymers' leaching behaviour. Indeed, Novais *et al.* [15] observed higher OH⁻ leaching in the first 10 days when increasing the porosity of geopolymer monoliths, while with longer periods smaller differences in leaching were perceived between the compositions. Moreover, an increase in the average diameter of the spheres is also observed with rising pore forming agent content. The average diameter increases from 2.36 ± 0.10 mm (50RM_0.30) to 2.61 ± 0.20 mm (50RM_0.59). This greater diameter will affect the specific surface area of the spheres and, therefore, their leaching behaviour, and a higher specific surface area is expected to enhance alkalis leaching to the medium.

Fig. 6 presents SEM micrographs and EDS maps of two compositions, namely the lowest- and the highest-containing RM. The micrographs show the formation of a geopolymeric gel, while the EDS maps and the EDS elemental composition shows that

an aluminosilicate gel is formed. Other elements, such as Fe and Ca, were also detected. These results provide additional evidence of the geopolymerisation reaction [15, 23].

Nevertheless, and considering the significant CaO content (~ 22 wt.%) in the FA composition, the formation of calcium silicate hydrates (C-S-H) cannot be ruled out.

The XRD patterns of the RM-based geopolymer spheres are presented in Fig. 7. The shape of the patterns is similar, yet the intensity of some crystalline phases (e.g. calcite) decreases, while others increase (e.g. anatase and rutile), when the RM content in the composition rises. Not surprisingly, it was observed that changing the pore forming agent content does not affect the geopolymer mineralogical composition.

The microstructure of the various compositions of geopolymer spheres is shown in Fig. 8, while the EDS spectrum of the spheres' surface is presented in Fig. 9. The micrographs reveal the influence of both RM and pore forming agent on both the pore nature (open or closed), and volume of the produced pores. Increasing the RM content changes the nature of the pores produced, a denser microstructure being observed in the inner part of the spheres for higher RM content (60 wt.%), in comparison with that observed lower RM content (50 wt.%). The RM amount was also found to affect the sodium content in the geopolymer spheres, as depicted by the EDS spectrum shown in Fig. 9a, with an increase in the sodium content being observed when the RM content in the composition rises. This observation is attributed to the higher sodium content in the RM (4.82 wt.%) in comparison with the FA (1.68 wt.%), as demonstrated by the raw materials chemical composition (see Table 2).

Fig. 8b shows that the pore forming agent content controls the volume and size of the pores produced. With rising pore forming agent content, the volume and size of the pores increases. It was also observed that the sodium content on the surface of the spheres (see Fig. 9b) increases when increasing the pore forming agent amount. This

observation shows that higher porosity values promote alkalis migration/diffusion to the sphere surface, which is expected to strongly affect the pH buffering capacity of these materials.

Fig. 10 presents the cumulative OH⁻ ions leaching from the various geopolymers as a function of time, while the leaching percentage, calculated using equation (1), is provided in Fig. 11 to further characterise the leaching behaviour.

$$Leaching_j (\%) = \frac{\sum_{i=1}^j [OH^-]_i}{[OH^-]_{total}} \times 100 \quad (1)$$

Substantial differences in the OH⁻ leaching amount are perceived between the compositions immediately after the 1st day. Results show that the most significant factor influencing the spheres' leaching is their porosity, while the RM content plays a less relevant role. Interestingly, the lower porosity compositions leached a greater amount of alkalis in comparison with their higher porosity counterparts. For instance, 50RM_0.30 leached ~ 20 % more OH⁻ ions in comparison with 50RM_0.59 after 28 days. This unexpected behaviour conflicts with previous reports, that have observed higher leaching when the porosity of the bodies, presenting identical geometry, increases [15]. There are two possible explanations for this behaviour:

i) The lower porosity spheres have smaller diameters than those with larger porosity, as discussed above. Therefore, for each gram of tested spheres, we would expect the smaller spheres to have a proportionally larger total surface area, thus promoting higher alkalis leaching. As can be seen in Fig. 5, the spheres with less pore forming agent are not only smaller, but also more regular, and form a more compact mass. It can also be seen from this figure that, for the same number of spheres (12 in this case), those with more pore forming agent take up more volume.

ii) The greater degree of partial destruction/erosion of the higher porosity spheres during the leaching tests, which hindered their pH buffer ability. The latter is clearly visible in the optical micrographs shown in Fig. 12. The specimens' weight loss after leaching was also included in the figure, and is in line with the lower mechanical stability of the higher porosity spheres.

The specimens leaching percentage (see Fig. 11) was similar for all compositions in the first 7 days, while afterwards differences tend to increase. Higher porosity compositions (containing 0.59 g of pore forming agent) reached the maximum OH^- ions leaching earlier than their lower porosity counterparts, this meaning that these compositions reached exhaustion faster, and thus present lower pH buffering ability.

The maximum OH^- ions leaching here reported for the RM-based spheres ($0.0237 \text{ mol/dm}^3 \text{ g}$) was compared with other reported values, and results are presented in Fig. 13. In the work of Ascensão *et al.* [12], the authors presented the OH^- leaching in mol/dm^3 ; however for comparison purposes their OH^- leaching per gram ($\text{mol/dm}^3 \text{ g}$) was determined, considering the volume (8 cm^3) and bulk density (0.87 g/cm^3) of their specimens, and included in Fig. 13. The RM-based geopolymer spheres are only surpassed by the FA-based geopolymer spheres (25% higher leaching) reported by the authors [16], and by the glass powder modified alkali activated materials (12% higher leaching) [24]. The lower leaching of the RM-based spheres in comparison with the FA-based spheres [16] is explained by the substantially lower amount of alkaline activators ($\sim 18 \%$) used in the present investigation, while the glass powder modified alkali activated materials production required heat treatment (between 200 and 400 °C) [24]. The proposed methodology is, therefore, less expensive and environmentally friendlier than those reported in previous works. Moreover, the RM-based spheres show superior OH^- leaching than that of FA-based geopolymer monoliths (32%) [15], possessing

substantially higher (94%) leaching than the only previous study addressing the use of RM-based geopolymers (monoliths) for pH control [12]. These results clearly demonstrate the huge potential of the RM-based geopolymer spheres to act as pH regulators.

The distinct leaching behaviour of the RM-based geopolymer spheres affected their pH buffering capacity, as illustrated in Fig. 14. Composition 50RM_0.59 exhibited the worst pH buffering capacity among the investigated specimens, being exhausted after the 18th day. The latter was associated with the samples' poor stability/partial collapse during leaching tests. Specimens prepared with 40 and 60 wt.% RM behave slightly better, reaching exhaustion on the 21st day. The lower porosity spheres (containing 50 wt.% RM) presented the best pH buffering ability (see Fig. 14b), as observed by their prolonged and continuous OH⁻ leaching (see Fig. 10). After the 28th day, the pH decay was 2.4 and 2.6, respectively, for compositions 50RM_0.30 and 50RM_0.40. The pH fluctuation over time of the RM-based spheres is narrower than that reported for metakaolin-waste inorganic polymers (~ 4-5 [25] and ~ 3-4 [19]), and metakaolin-based geopolymer spheres (3.7 [16]), which demonstrates the potential of the RM-based spheres as pH regulators. Other studies have reported lower pH decay over time: 1.6-1.9 for FA-based spheres [16], ~ 0.9-1.5 for FA-containing monoliths [15], and 1.6-2.1 for RM-based geopolymer monoliths [12]. Nevertheless, these studies used higher alkaline activator contents in comparison with the present investigation, which is less environmentally friendly.

The pH buffer ability of the RM-based spheres shown in aqueous medium suggests the possibility of using them as pH regulators in the anaerobic digestion of organic waste. The possibility of using FA-based geopolymers to control the pH and promote methane production in batch operated anaerobic reactors has been recently demonstrated by the

authors [22]. The use of RM-based spheres to control the pH of anaerobic digesters may boost the generation of renewable energy (e.g. methane), which is a hot topic nowadays due to the demanding directives of the European Commission regarding energy production from renewable sources [26]. The envisioned use of RM-based geopolymers as pH regulators in anaerobic digestion may significantly reduce RM waste disposal, while contributing value to this unexplored waste material. Nevertheless, considering the massive accumulated global red mud stockpile, other valorisation solutions must be implemented. One exciting possibility is the use of these red mud-based spheres as low cost adsorbents in wastewater treatment systems. Indeed, the high market demand for low cost adsorbents suggests that high red mud contents could be reused. However, further studies must be performed to immobilise the toxic elements present in the red mud composition.

The leaching of iron, chromium and lead from the specimens during their immersion in water was evaluated, and results shown in Table S1 (provided as Supplementary Material). Despite the significant content of iron present in the red mud (~ 52 wt.%), iron was not detected in the water solution even after 28 days immersion. Results also show that a small amount of chromium (0.2065 ppm) leached from the spheres after the first immersion day, while afterwards no further chromium leaching was observed. An even smaller amount of lead, ranging from 0.0095 to 0.1457 ppm, was detected in the water. These values are not expected to present any inhibitory effect in anaerobic digestion. In fact, the addition of trace elements (heavy metals), such as Fe, Ni, Cu, Zn and Co, among others, has been found to enhance methane production [27, 28], while its absence is detrimental to anaerobic processes [29]. Recently, red mud was used to improve the methanogenesis during sludge anaerobic digestion [30]. In this reference, red mud was used as a powder, while in our investigation red mud was chemically

activated to generate geopolymer spheres. Therefore, the metals leaching potential is severely reduced when using spheres with stabilised red mud in comparison with their use as untreated powder. Future work will address the use of red mud-based spheres in anaerobic digestion, and the influence of heavy metal leaching will also be considered. The use of red mud-based geopolymer spheres in wastewater treatment systems requires further optimisation to immobilise the heavy metals in the geopolymeric framework, hence preventing their leaching from the spheres.

To further characterise the RM-based spheres after leaching tests, SEM analysis was performed on the best performing compositions (50RM_0.30 and 50RM_0.40), and results are shown in Fig. 15. The SEM micrographs show an increase in their porosity after the leaching tests (28 days), with several cracks in the surface being evident. Moreover, the EDS spectra (Fig. 15b) show a major reduction in the sodium content, in line with the observed exhaustion of the spheres. Nevertheless, the spheres preserved their integrity, which may allow their reuse after exhaustion in other applications such as heavy metal [31] or dye adsorbent [32], further contributing to the circular economy concept.

4. Conclusions

In this work, and for the first time, RM-based geopolymer spheres were synthesised and then evaluated as pH buffering materials. The influence of RM and pore forming agent content on the OH⁻ ions leaching over time was investigated. Geopolymer spheres containing up to 60 wt.% RM were successfully produced - higher contents were found to negatively affect the geopolymers spherical shape.

Results show that the spheres' porosity was the most significant factor affecting the alkalis release, while the RM content showed a less relevant role. Decreasing the pore

forming agent amount increased the spheres mechanical stability which allowed a prolonged OH^- leaching and narrow pH decay (2.4 pH units) over time.

The maximum alkalis leaching here observed ($0.0237 \text{ mol/dm}^3 \text{ g}$) is among the highest ever reported for geopolymers, being roughly twofold higher than that only other study addressing RM-based geopolymers, clearly demonstrating the improved performance of the RM-based spheres. The RM-based spheres maximum leaching is only surpassed by systems where higher alkaline activators content or heat treatment was employed, and for that reason the here proposed strategy is more eco-friendly and cost-effective. These results suggest the possibility of using the RM-based spheres to control pH in anaerobic digesters, which due to the renewed interest in biogas production using this technology may allow the valorisation of significant amounts of this hazardous and unexplored waste material. Furthermore, the spheres were produced using solely waste materials (RM and FA) as silica and alumina sources, which further reduces the geopolymers' production cost, in comparison with those produced using benchmark materials, such as metakaolin.

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Figures:

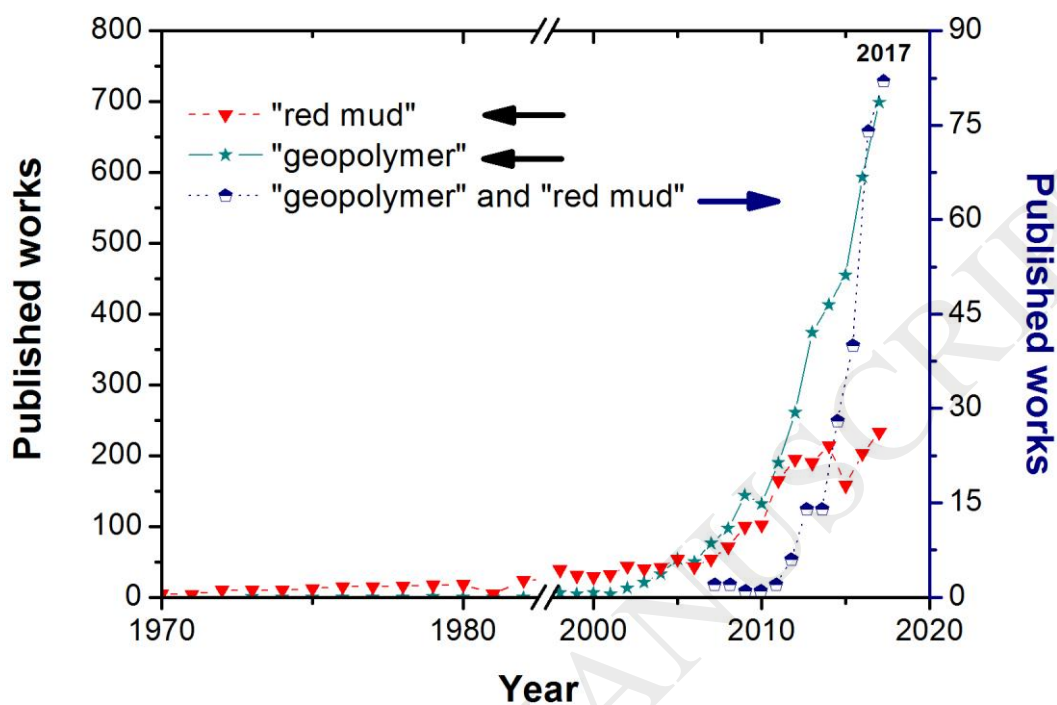


Fig. 1 Number of works published for “red mud”, “geopolymer” and “geopolymer and red mud” (Data obtained from Scopus on 29 December 2017).

Note that (“geopolymer” and “red mud”) corresponds to the much smaller scale on the right-hand y-axis.

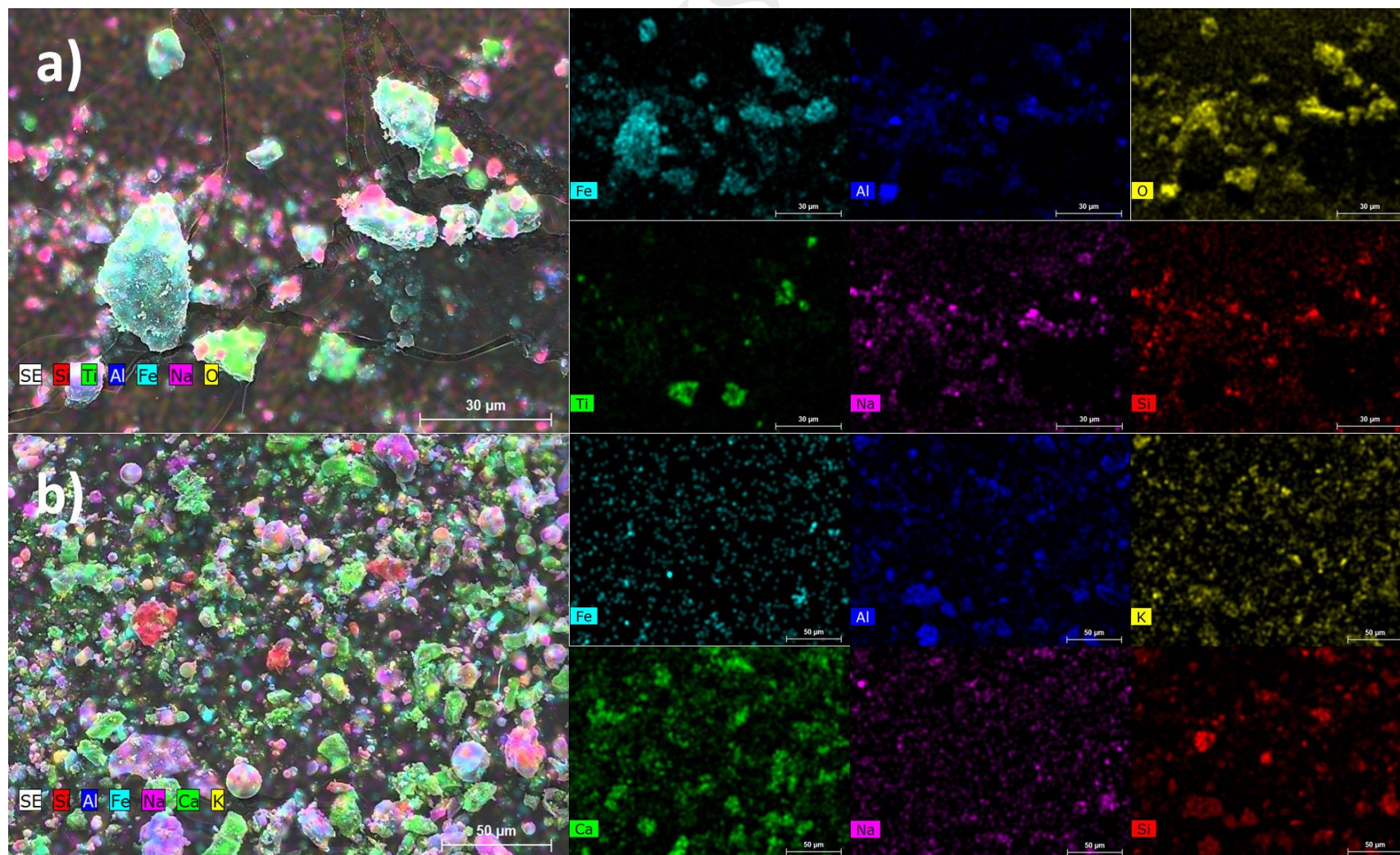


Fig. 2 EDS elemental mapping of a) red mud and b) fly ash particles.

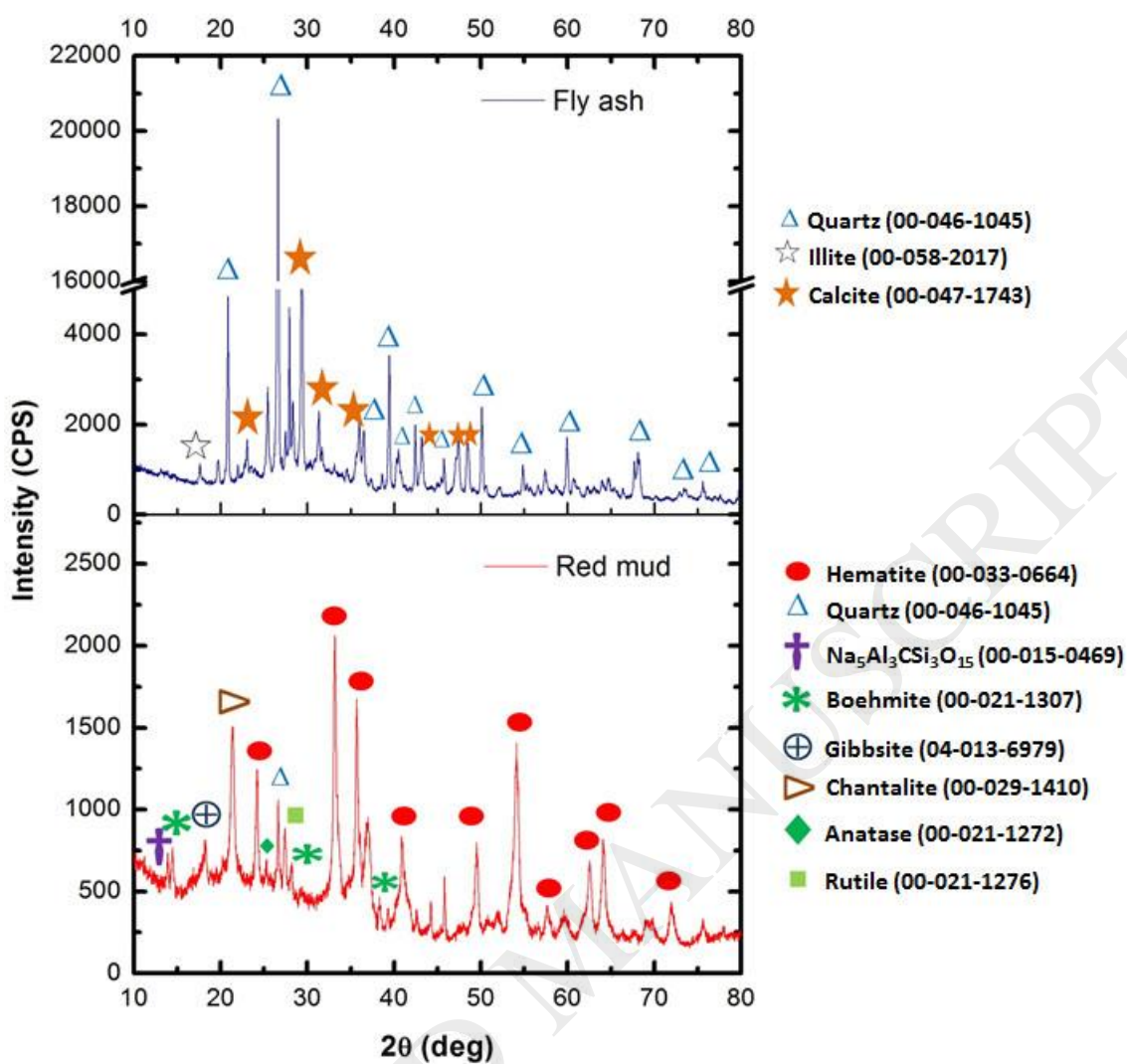


Fig. 3 XRD patterns of the aluminosilicate precursors: fly ash and red mud.

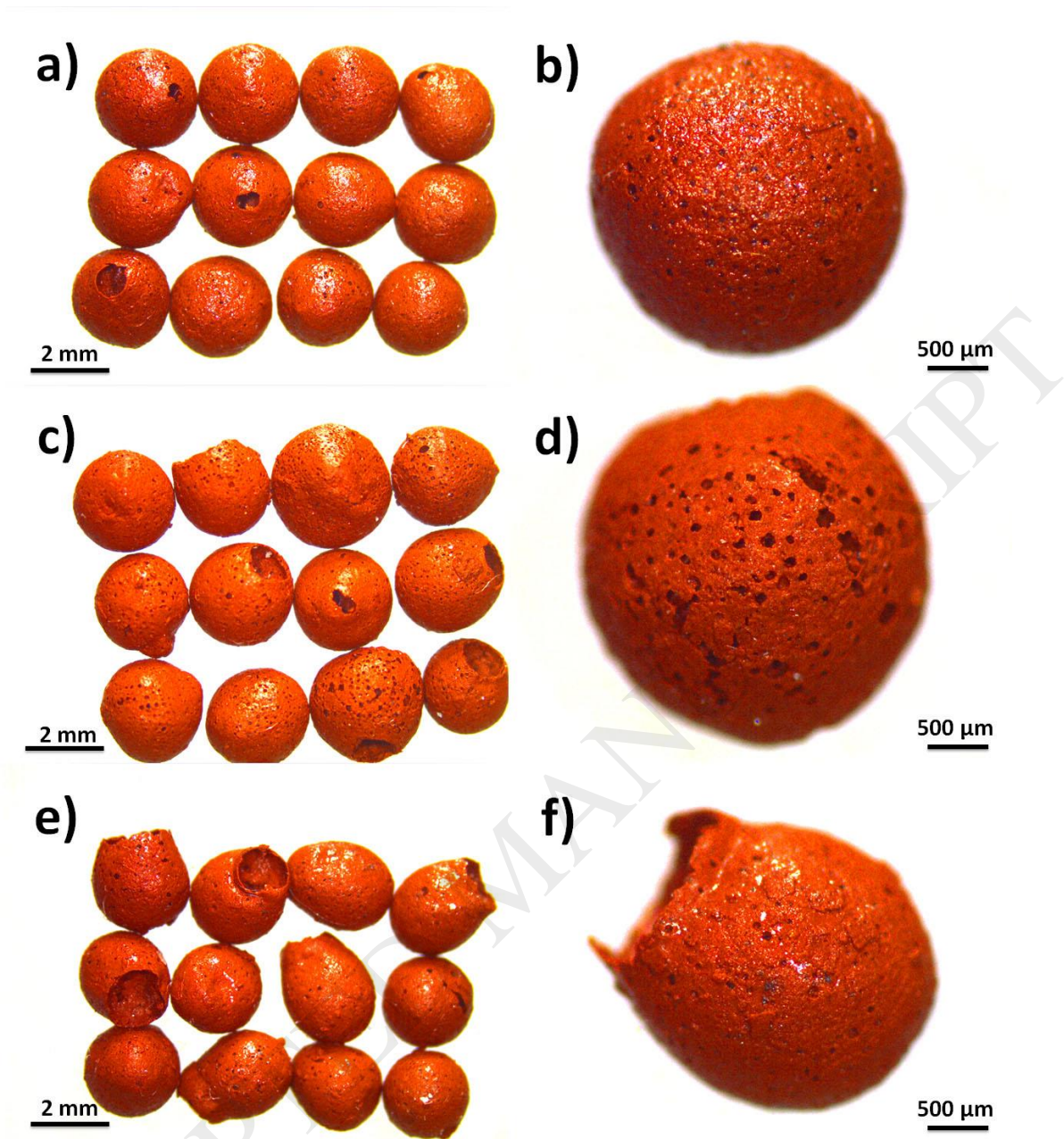


Fig. 4 Optical characterisation of the red mud-containing geopolymer spheres with varying amounts of red mud: (a, b) 40 wt.%, (c, d) 50 wt.% and (e, f) 60 wt.%.



Fig. 5 Optical characterisation of the red mud-containing geopolymer spheres prepared with varying pore forming agent content: a) 0.30 g, b) 0.40 g and c) 0.59 g.

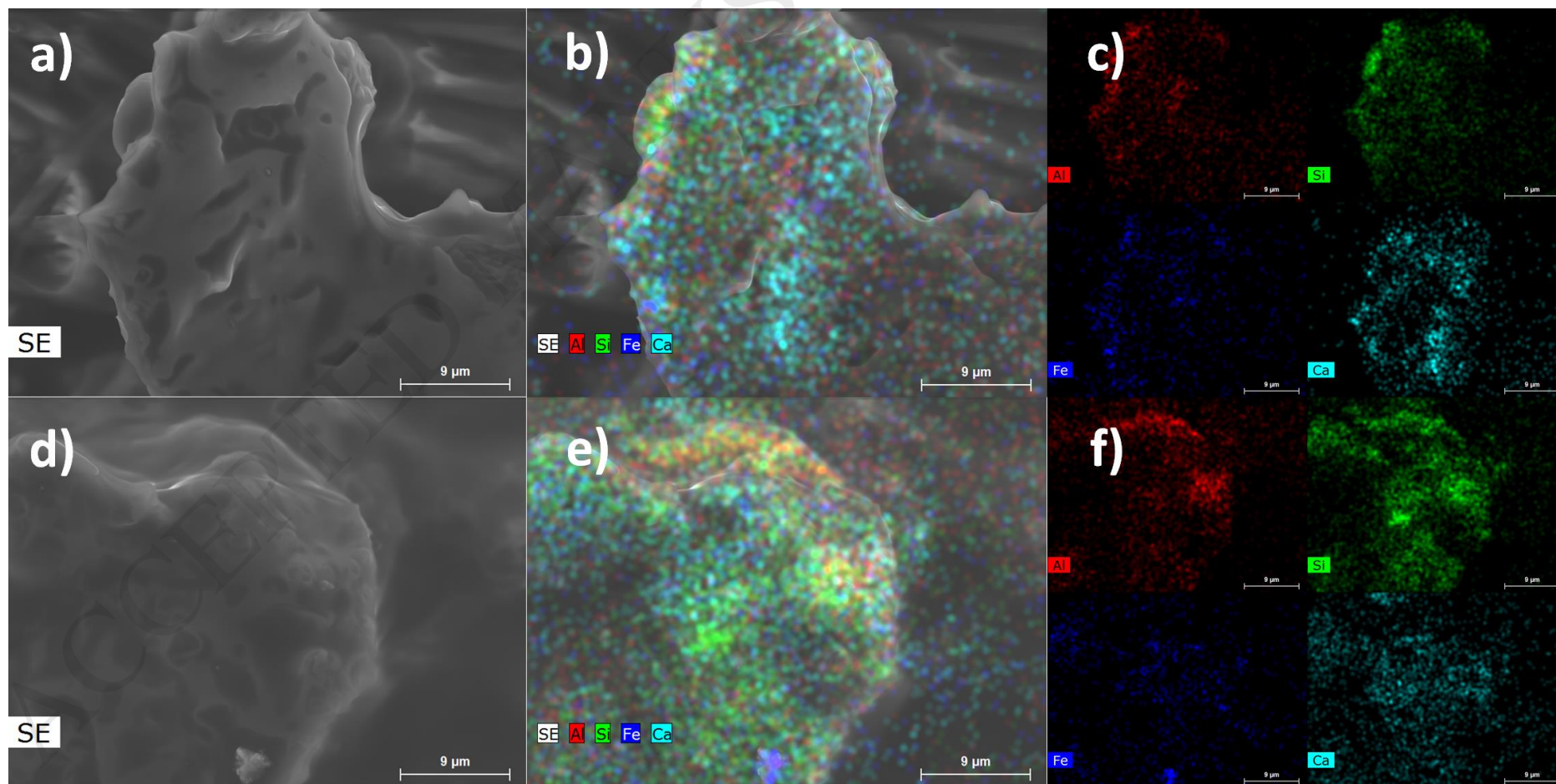


Fig. 6 SEM micrographs (a, b) and EDS maps (b, c, e, f) of the compositions (a-c) 40RM_0.59 and (d-f) 60RM_0.59.

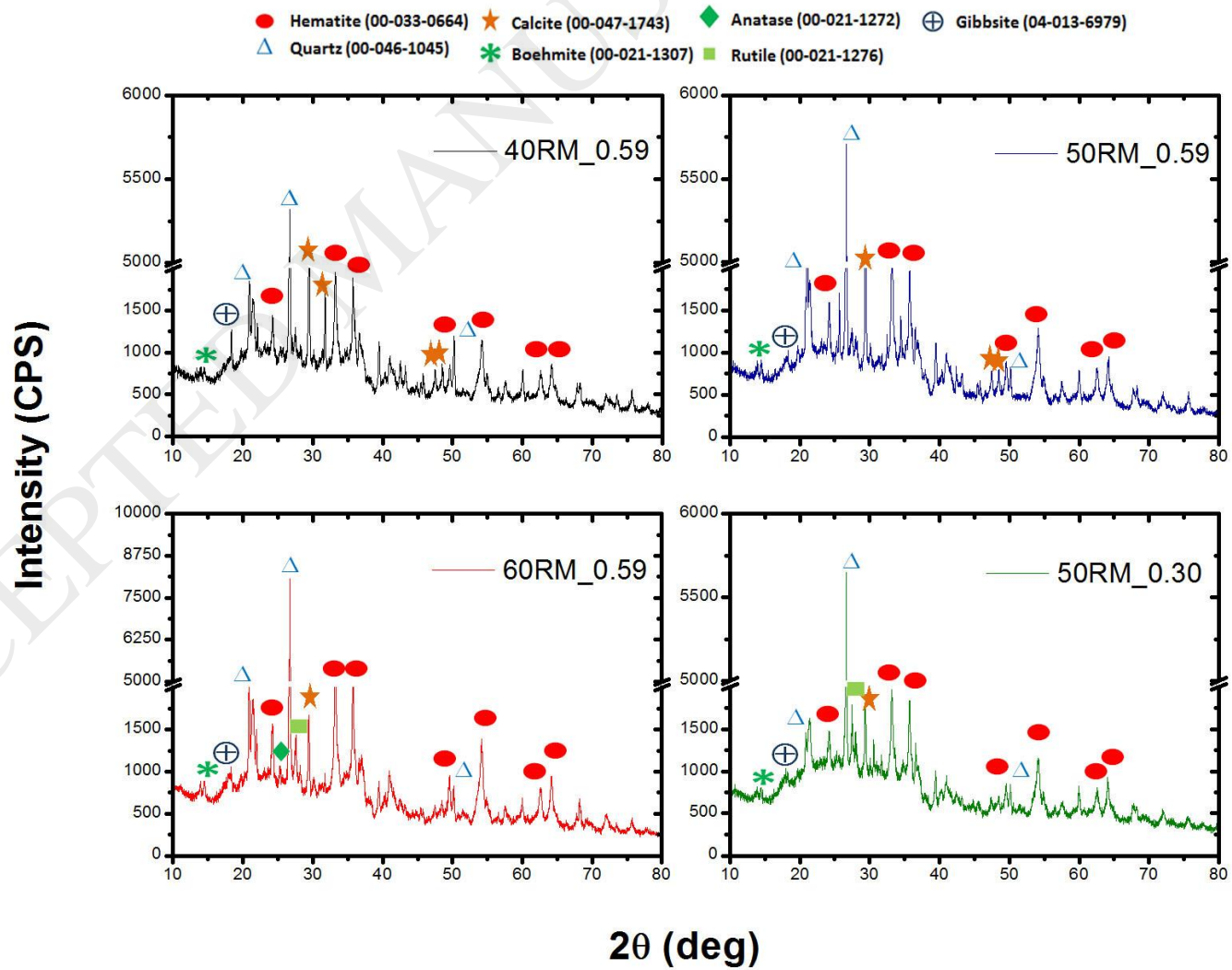


Fig. 7 XRD patterns of red mud-containing geopolymeric spheres.

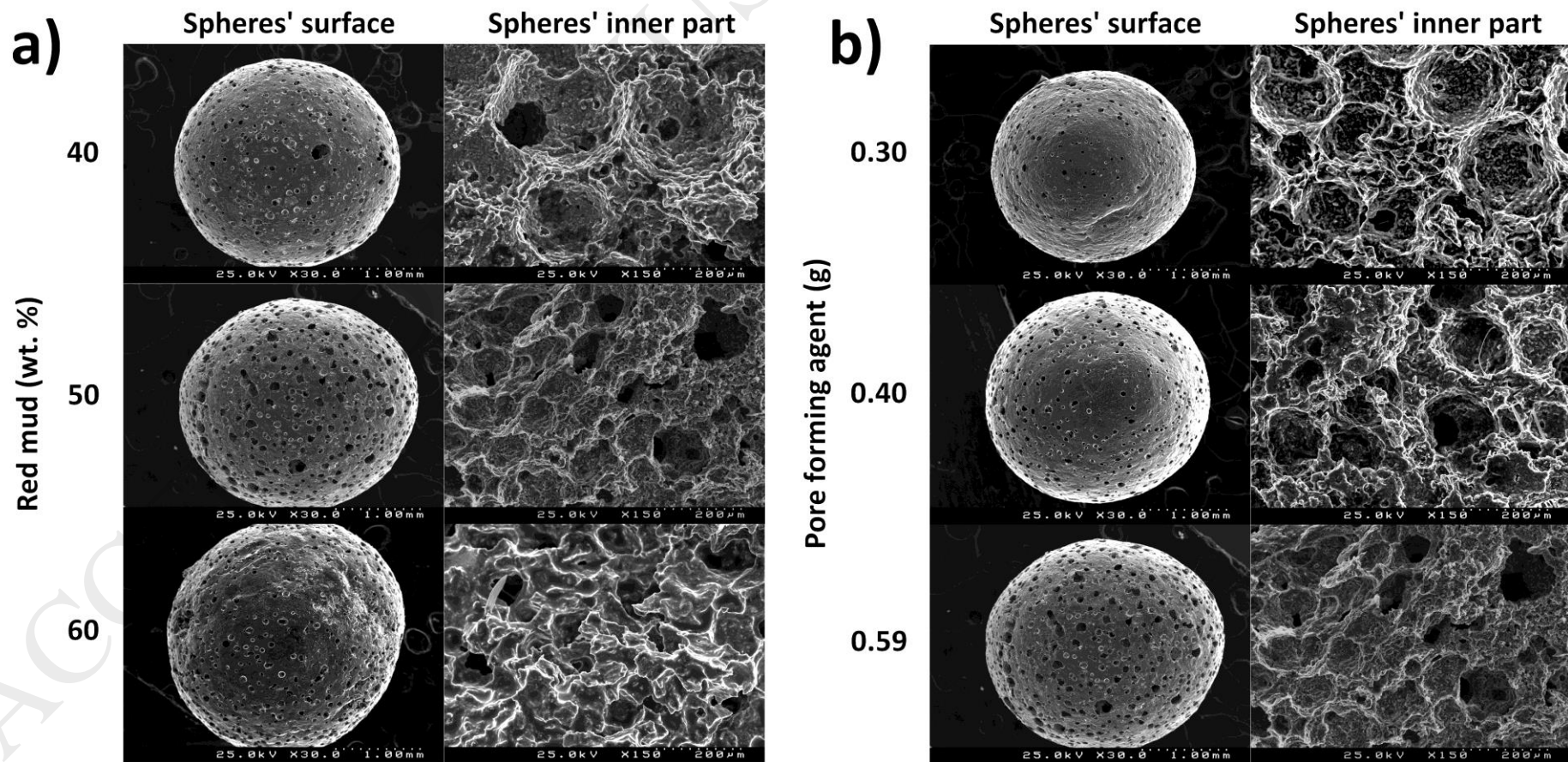


Fig. 8 SEM characterisation of the red mud-containing geopolymeric spheres prepared with: a) varying red mud content (0.59 g pore forming agent) and b) varying pore forming agent content (50 wt.% red mud).

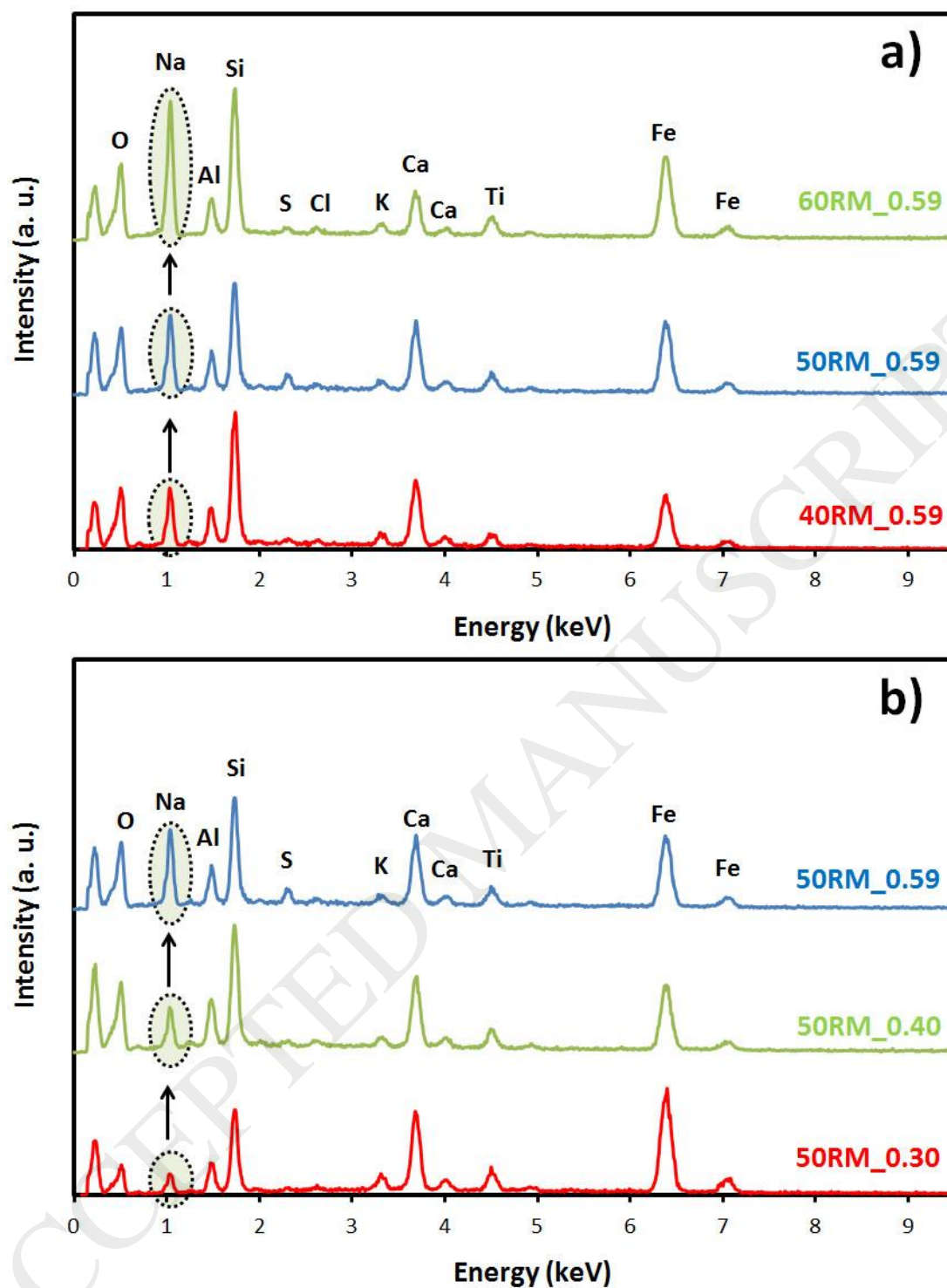


Fig. 9 EDS spectra of the geopolymeric sphere surfaces prepared with: a) varying red mud content (0.59 g pore forming agent) and b) varying pore forming agent content (50 wt.% red mud).

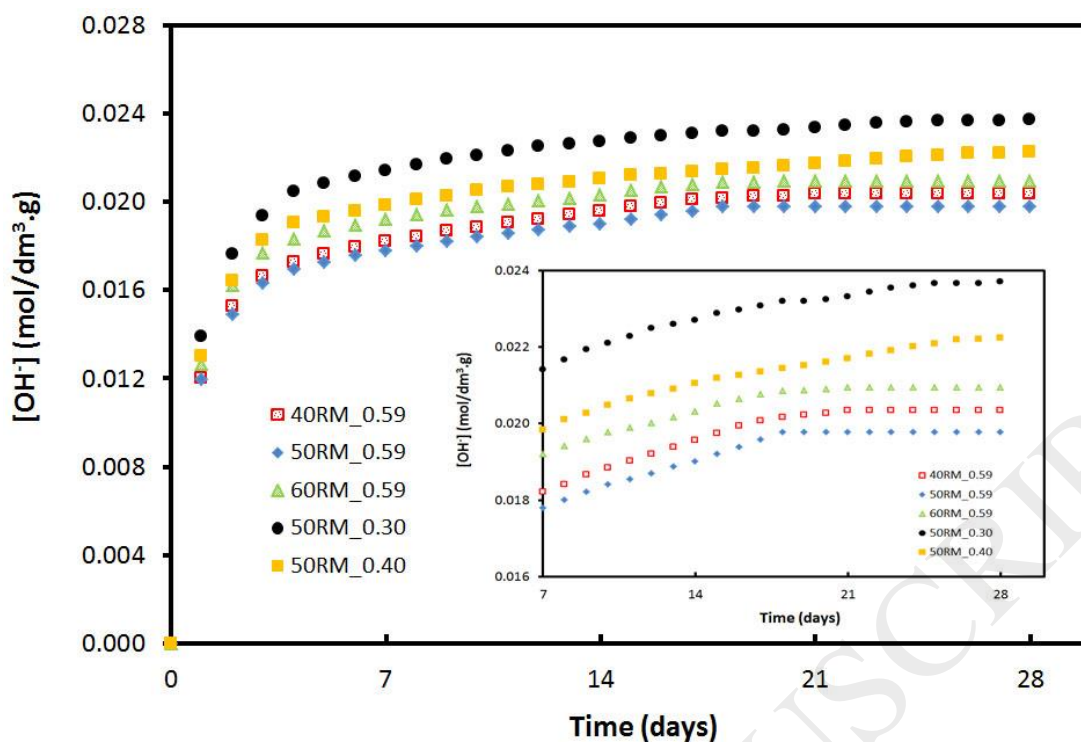


Fig. 10 Cumulative leaching of OH^- ions from the red mud-containing geopolymer spheres. The inset graph illustrates the OH^- leaching between the 7th and the 28th day.

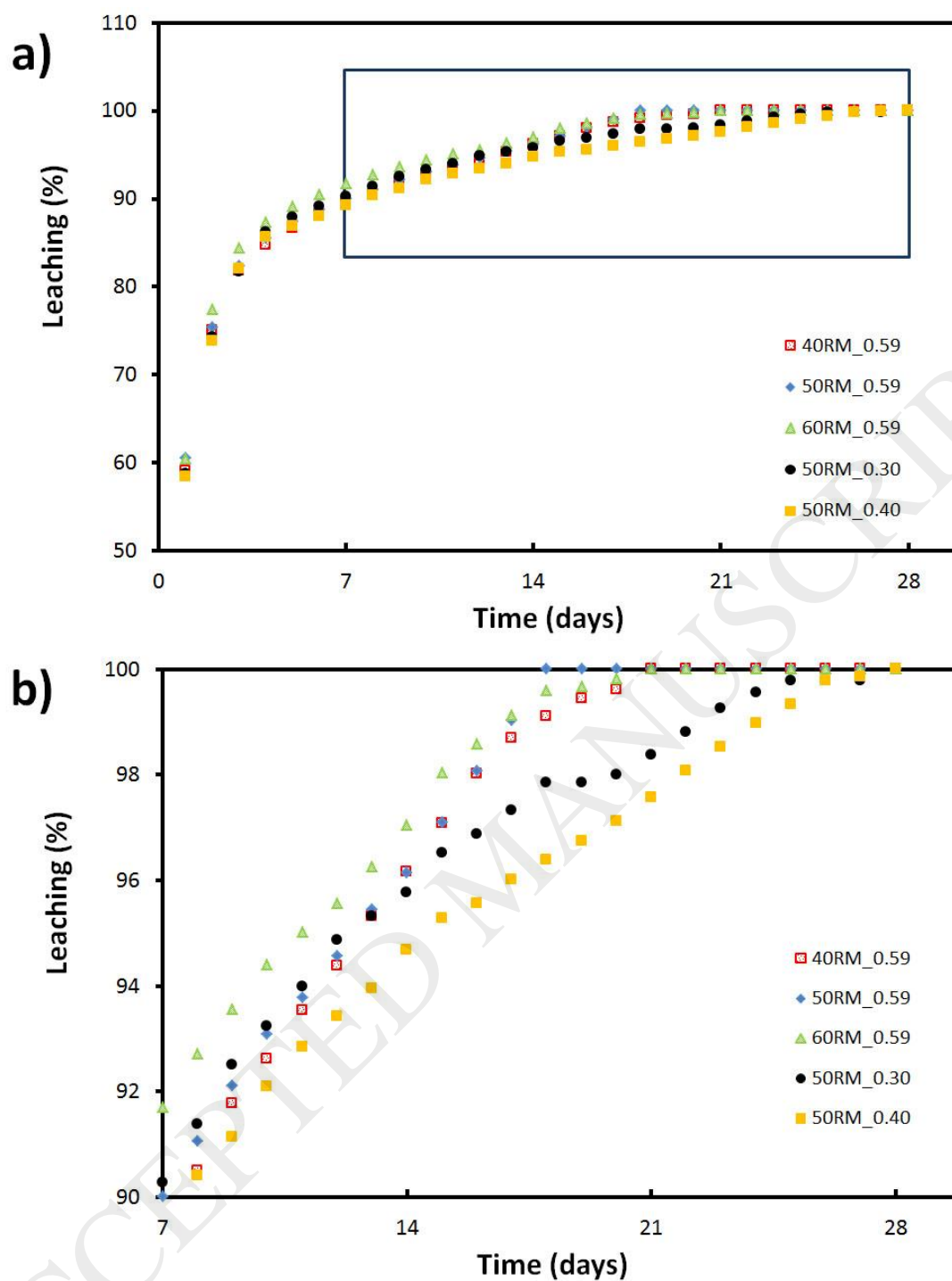


Fig. 11 Leaching percentage of OH^- ions from the red mud-containing geopolymer spheres. Fig. 10b corresponds to the leaching percentage highlighted in Fig. 10a, further illustrating the leaching rate over time.

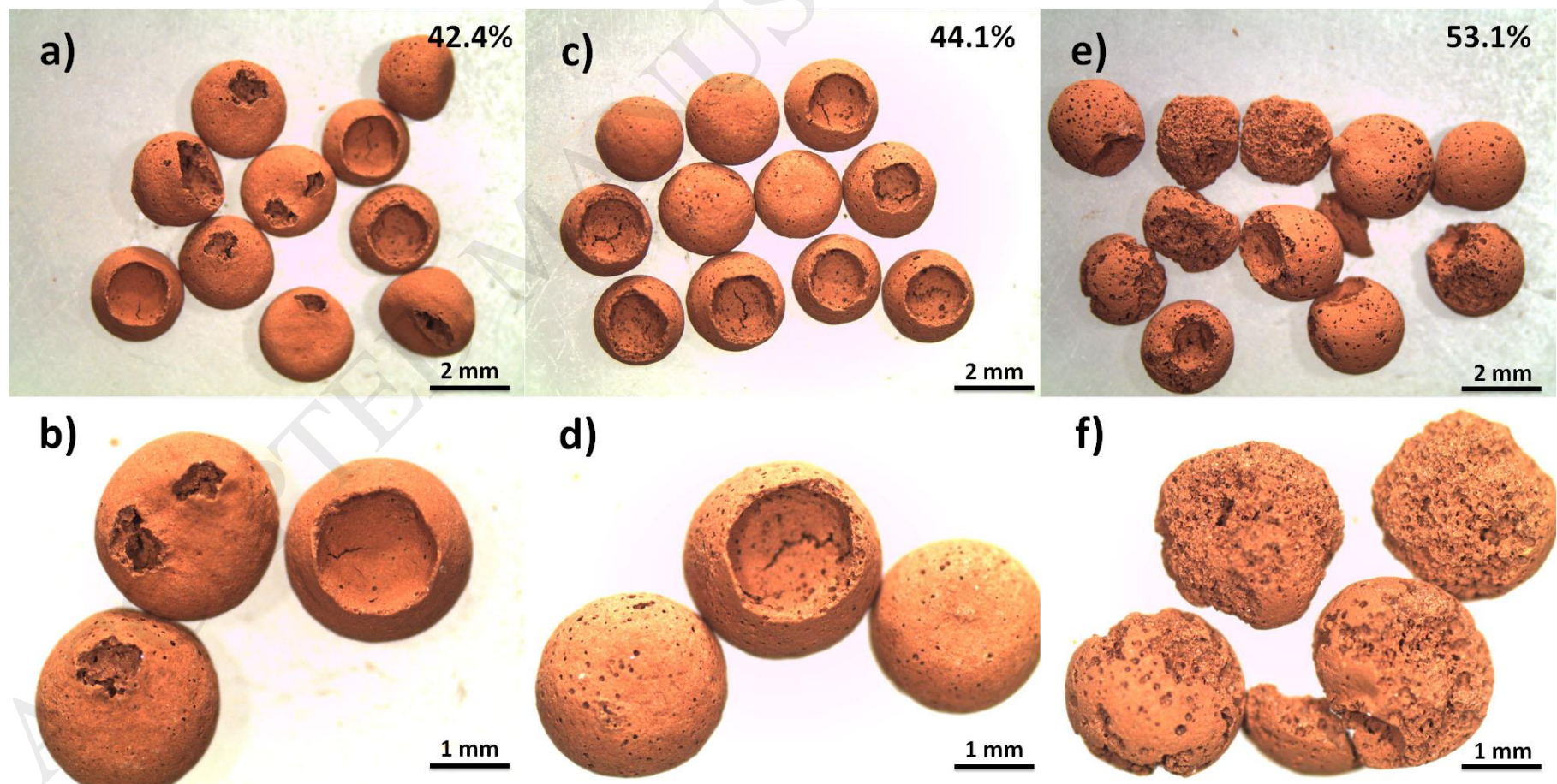


Fig. 12 Optical characterisation of the red mud-containing geopolymer spheres (50RM) prepared with varying pore forming agent content after leaching tests (28 days water immersion): (a, b) 0.30 g, (c, d) 0.40 g and (e, f) 0.59 g. The specimens' weight loss (wt.%) after leaching is indicated above the micrographs.

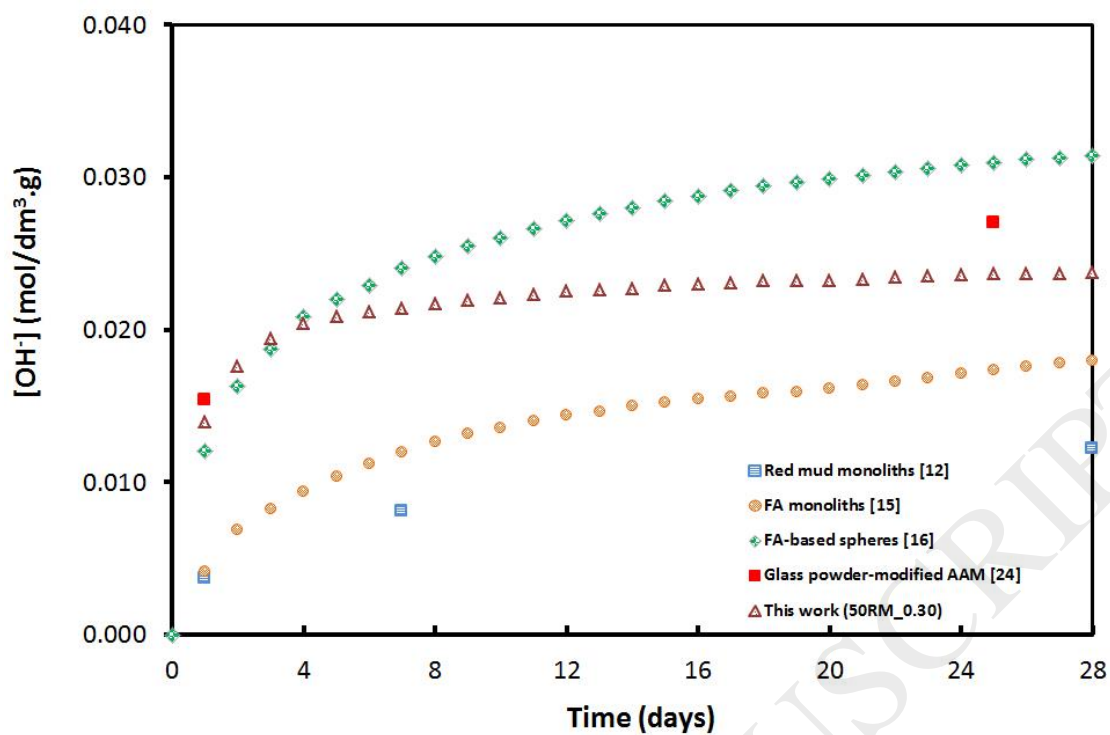


Fig. 13 Comparison between the cumulative leaching of OH^- ions obtained for composition 50RM_0.30 with data from other investigations reported in literature.

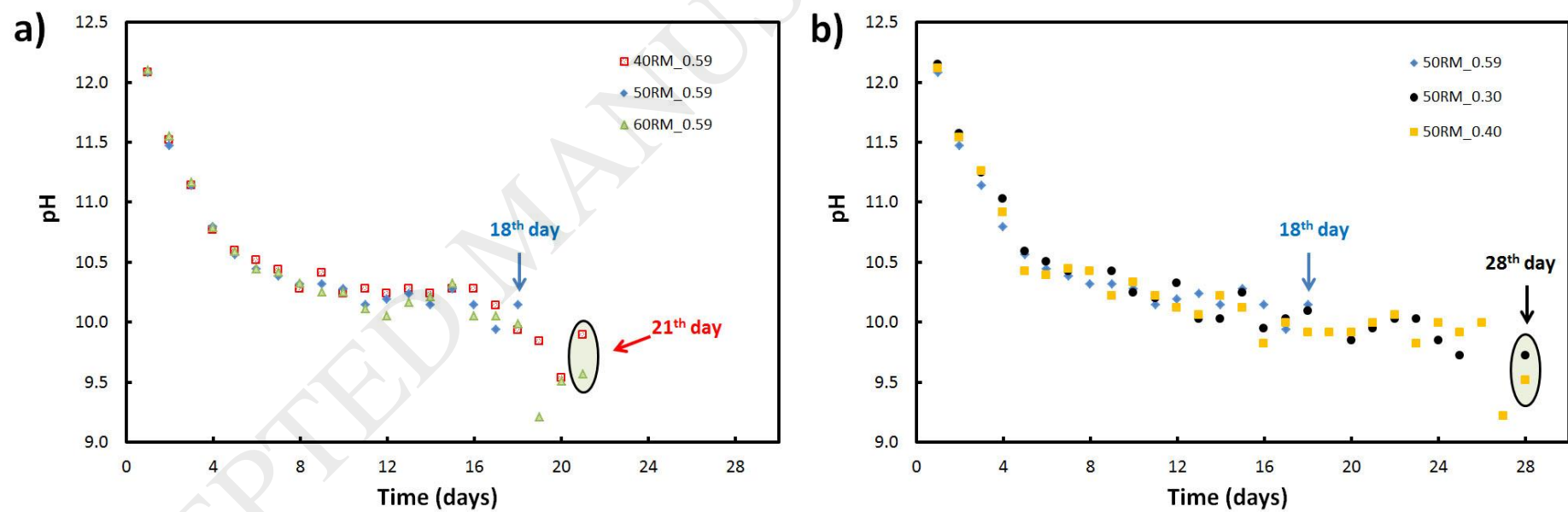


Fig. 14 pH of the water solution after geopolymer spheres immersion as a function of time: a) influence of red mud content and b) pore forming agent amount.

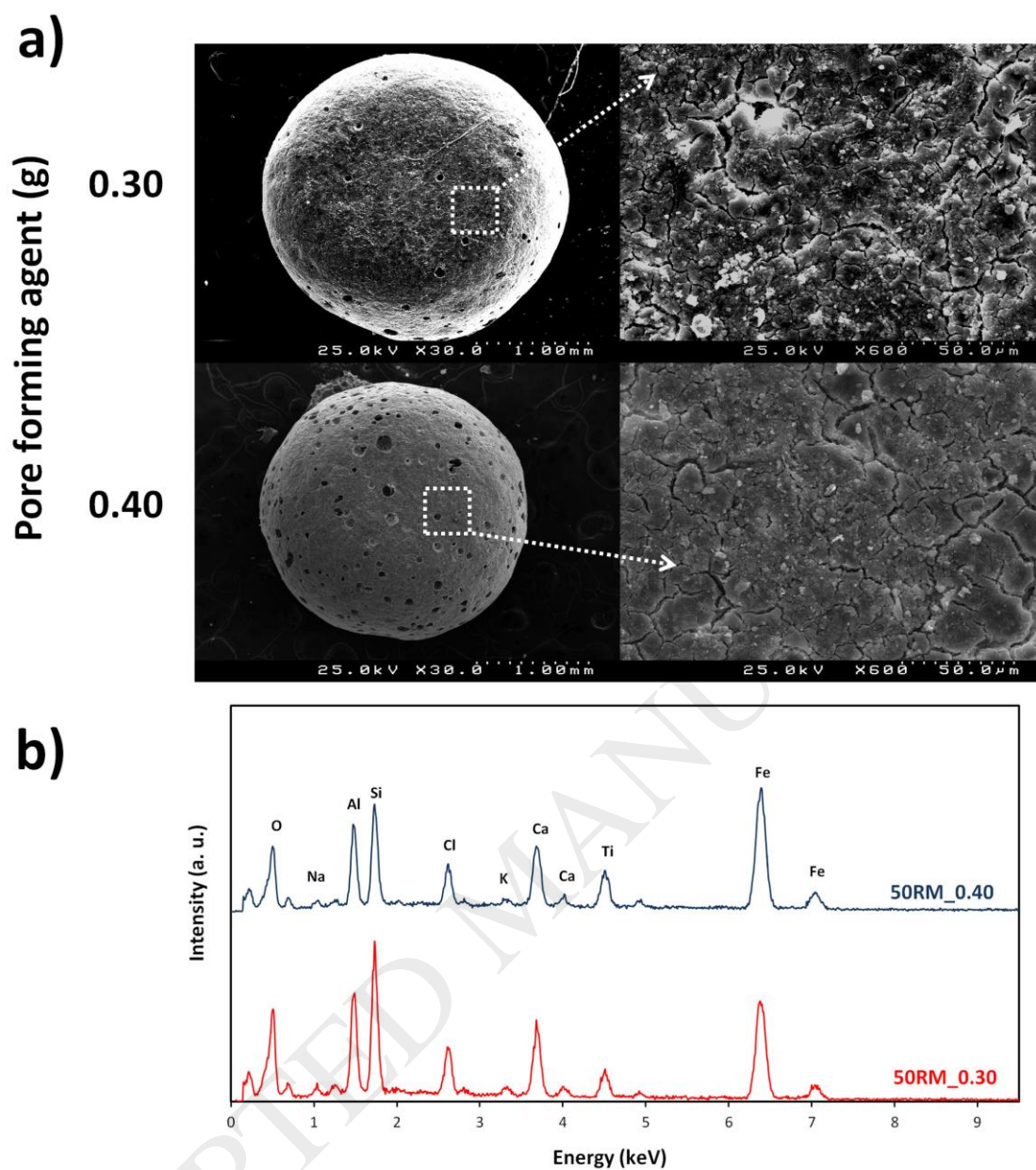


Fig. 15 a) SEM characterisation and b) EDS spectra of the red mud-containing geopolymer spheres after leaching tests.

Tables:**Table 1** Geopolymer preparation: mixture composition.

Sample name	RM content (wt.%)	Mixture proportion (g)				
		RM	FA	Alkaline activator	H ₂ O	Foaming agent
40RM_0.59	40	8	12	15	4.15	0.59
50RM_0.59	50	10	10	15	4.15	0.59
60RM_0.59	60	12	8	15	4.15	0.59
50RM_0.40	50	10	10	15	4.15	0.40
50RM_0.30	50	10	10	15	4.15	0.30

Table 2 Raw materials chemical composition obtained by XRF. LOI = loss on ignition.

Oxides (wt.%)	RM	FA
SiO ₂	5.67	33.13
TiO ₂	9.41	0.71
Al ₂ O ₃	14.63	13.31
Fe ₂ O ₃	52.25	5.32
MgO	0.08	3.35
CaO	1.88	22.20
MnO	0.06	0.57
Na ₂ O	4.82	1.68
K ₂ O	0.08	5.67
SO ₃	0.32	3.87
P ₂ O ₅	0.53	1.25
LOI	9.44	7.05