Reaction kinetics and structural analysis of alkali activated Fe-Si-Ca rich materials

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ABSTRACT

This paper describes the outcomes of a study conducted to investigate the influence of solid-to-liquid (S/L), K_2O/SiO_2 molar ratio and type of activation solution on reaction kinetic, structural development and final mechanical properties of Fe-Si-Ca rich inorganic polymers (IP). IPs were synthesized with alkali hydroxide and alkali hydroxide/silicate type activators to investigate the kinetic and structural impact of soluble silicates on the activating solution. Multiple characterization techniques, including isothermal conduction calorimetry (ICC), X-ray diffraction (XRD) and infrared spectroscopy (FTIR), were used to give insights on the impact of each of the considered synthesis parameters. Solid-to-liquid and K_2O/SiO_2 ratios were found to be the compositional parameters governing the reaction kinetics, whereas the introduction of silicate species in the activating solution contributed to further densification and strength development. By combining the effect of the studied parameters, IP binders incorporating a high content of a Fe-Si-Ca rich residues (≥ 92.7 wt% of solid content) were synthesized at room temperature to achieve a compressive strength exceeding 119MPa. This work contributes with new insights into the reincorporation and upscaling of a vast group as yet unexplored Fe-Si-Ca-rich waste streams into the materials cycle, such as non-ferrous slags and vitrified residues generated during the incineration of municipal solid waste or during the gasification refused-derived fuel. The study demonstrates the feasibility of producing high strength IPs with only minor usage of virgin raw materials and the possibility of using the developed products as an alternative to conventional cementitious binders. Promoting synergetic interactions between proxy industries is crucial to the sustainability of our current production processes and will play a critical role in achieving current environmental targets.

Keywords: Fe-Si-Ca rich inorganic polymers; reaction kinetics; reaction products; upcycling

1. INTRODUCTION

Over the course of the twentieth century, anthropogenic activities have led to the near exhaustion of certain natural resources, e.g. water (Mekonnen, 2016; World Economic Forum, 2018), metals, non-metallic minerals and biomass (Kuipers, 2018). Resource shortages require a paradigm shift and development of innovative, sustainable upcycling solutions is now crucial. In this context, landfills can be considered as resource stocks, and their future mining has attracted substantial attention (Jones, 2013; Krook, 2012). Enhanced landfill mining (ELFM) is an integrated process with which to recover valuable resources from landfill sites, with the aim of full valorization of waste streams, including upcycling by-products generated during the ELFM process (Jones, 2013). Sorting techniques allow direct recovery of some waste fractions (e.g., metals, glass and aggregates), whereas the remaining fraction is often thermally converted into energy (Danthurebandara, 2015). The gasification/vitrification of refuse-derived fuel (RDF) obtained via ELFM is emerging as a promising technology with which to convert such intermediate products into synthetic gas (syngas) and to transform the residual inorganic solid compounds into an inert vitrified material (commonly termed plasmastone) (Bosmans, 2013). Thus, as gasification technologies reach maturity and are implemented worldwide, significant volumes of these Fe-Si-Ca-rich vitreous residues are expected to be generated and large-scale valorization routes still need to be developed. The need to develop strategies to reintegrate large volumes of Fe-Si-Ca-rich residues into the materials cycle is further exacerbated when considering that similar wastes are also produced in the pyrometallurgical sector and during the incineration of

municipal solid wastes. Currently, use of those residues is limited to low-value applications (e.g. road paving) and the majority of these residues end up being either landfilled or stockpiled. Yet, if a rapid solidification stage is introduced during the production process, either by water quenching or dry granulation, Fe-Si-Ca rich residues can present a predominantly amorphous structure that suggests their suitability for being used as inorganic polymer precursors (further abbreviated as IPs) as one possible large-scale valorization route. The potential of alkali activation of these glassy materials has been recently addressed with promising results. Suggested applications include pavers (Machiels, 2017), mortars (Machiels, 2014) and insulating materials (Kriskova, 2017). Despite the success of those studies in developing Fe-Ca-rich IPs suitable for such applications, there remain significant unknowns regarding the synthesis parameters that control the reaction kinetics and the products formed. Further insight into the latter is crucial to be able to properly engineer the IPs' structures and final properties, and to estimate their long-term performance. In the case of RDF vitreous residues, comprehensive knowledge of alkali-activation mechanisms is particularly important as the glass phase chemistry and mineralogy are largely dependent on the vitrification process, feedstock materials (industrial and/or urban solid waste), age (fresh or landfilled waste), geographic origin and applied pre-concentration/separation method (Bosmans, 2013). Systematic studies to assess the influence of such fluctuations on the reaction kinetics and structural evolution of the IPs produced downstream are scarce, and in-depth research is needed to develop robust and resilient mix designs able to accommodate such variability.

Combining multiple characterization techniques - isothermal conduction calorimetry (ICC), X-ray diffraction (XRD) and infrared spectroscopy (FTIR) - to analyze reaction kinetics and the products formed upon alkali activation has previously provided

valuable insights on metakaolin (Zhang, 2012; Zhang, 2013), GGBFS (Gebregziabiher, 2015) and fly-ash based systems (Zhang, 2014). Yet, each aluminosilicate-rich material exhibits its own dissolution and hardening mechanism once alkali-activated, depending on its mineralogical and chemical composition (Duxson, 2007) and particle fineness (Marjanović, 2014). The considerable Ca and Fe content of RDF-slugs significantly modifies the reaction kinetics, which challenges accurate prediction of the reaction products. Van Deventer *et al.* (2007) reported that Ca^{2+} and $\text{Fe}^{2+/3+}$ cationic species rapidly dissolve and precipitate, providing a large number of extra potential nucleation sites. The accelerating effect of higher Ca amounts can result in the removal of the OH^- ions from the solution, which has a net effect of lowering the pH. A decrease in the solution pH will affect the further dissolution/precipitation rate and reduce the solution supersaturation levels. These competing effects hamper the definition of a general reaction kinetic model for Fe-Ca-rich IPs, but Salman *et al.* (2015) observed very early exothermic peaks and concluded that these may be related to enhanced reaction kinetics due to the hydrolysis of Si-O-Ca and Ca-O-Ca linkages. Daux *et al.* (1997) showed that, under slightly alkaline conditions, the precipitation of dissolved Fe was much faster than Si and Al, which can also lead to a considerable pH decay and result in slower reaction progressions. However, the use of Ca-rich admixtures in Fe-rich IPs was shown to further accelerate the reaction kinetics, but to reduce the reaction extension (Beersaerts, 2019). In addition to the availability of Ca and Fe species and their impact in the dissolution stage, the reaction kinetics, phase development, and IP final properties are also insignificantly influenced by: the precursor to activating solution ratio (Ascensão, 2018); the activator nature (Zhang, 2012); and its molar concentration (Machiels, 2014). Therefore, understanding the basic principles and dominant compositional factors affecting the reaction kinetics of Fe-Si-Ca rich IPs, the products

formed and the IPs' performance is fundamental to the development of upscaling strategies for these abundant residues. Hence, this study investigated the influence of three main compositional parameters - solid-to-liquid; K₂O/SiO₂ molar ratio; and type of activation solution - on reaction kinetics, structural development and final mechanical properties of Fe-Si-Ca rich inorganic polymers. This paper reports on the production of an innovative waste-based material and offers valuable insights in to how such compositional parameters affect its production and final properties. In the context of increased production of Fe-Si-Ca-rich residues worldwide, this work contributes to the development and incentivization of new large-scale valorization routes by defining robust mix designs and, by doing so, establishing resilient production processes in which Fe-Si-Ca rich IP binders' properties can be tailored solely by controlling the studied parameters. Additionally, the produced IP materials have shown adequate properties for use in the construction sector, with potential application as a replacement for cementitious binders and, thereby, increased sustainability of the construction sector.

2. EXPERIMENTAL PROGRAM

2.1. Materials

To mimic the vitreous material produced in thermal conversion processes, a synthetic glass (plasmastone; hereafter PS) was produced and used as the IPs' main precursor. The glass was produced as described by Machiels *et al.* (2017). The PS was dried, homogenized and milled; it was composed of SiO₂ 35.1, CaO 22.9, Fe₂O₃ 22.8, Al₂O₃ 16.1, MgO 1.4, K₂O 0.6, TiO₂ 0.6, Na₂O 0.3, Mn₂O₃ 0.1, SO₃ 0.1 and 1.9% loss on ignition (LOI). XRF experiments do not allow the identification of different oxidation stages, and Fe₂O₃ content should be understood as PS total iron content. PS

particle size distribution is given in **Fig. 1**) and its BET surface area was determined to be 1120 m²/kg.

Densified silica fume (hereafter SF; Microsilica Grade 940, ELKEM®, Norway) was used as an admixture (wt% ≤5.2) to provide a secondary source of SiO₂ and to adjust the binders' theoretical molar ratios (assuming complete dissolution). SF was determined to be composed of (in wt%) 95.0 SiO₂. Minor elements such as CaO, Fe₂O₃, and Al₂O₃ were considered negligible (<0.5 wt%). The specific surface area of the SF was measured using the BET method and found to be 22210 m²/kg. Potassium hydroxide (14M) and potassium silicate solutions (23.8 wt% SiO₂, 9.5 wt% K₂O and 66.7 wt% H₂O) were prepared by dissolving potassium hydroxide beads (reagent grade, 85%, Carlo Erba, Italy) and anhydrous potassium silicate (-48 mesh; 2.5 SiO₂:K₂O wt%, Alfa Aesar, Germany) in demineralized water. K-type solutions were selected as K⁺ ions are known to promote slower reaction kinetics and greater oligomer connectivity, thus favoring the formation of more stable three-dimensional architectures, which also leads to higher mechanical performances compared to their Na⁺ counterparts (Poulesquen, 2011).

2.2. Methods

X-ray fluorescence (Bruker AXS S8 Tiger spectrometer) was used to determine the chemical composition of the raw materials. IPs' mineralogical composition was assessed by X-ray diffraction (XRD), conducted on a Bragg-Brentano configuration, Bruker D8 Advance diffractometer, equipped with LinxEye detector (Cu K α radiation $\lambda=1.54059$ Å, divergence slit 0.5°, Soller slit set 2.5°+2.5°, 5-70°2 θ , step/size 0.02° and t/step 0.04s) and phase identification by EVA software. The precursors' particle size distribution was determined by a laser particle analyzer (Malvern Mastersizer 3000),

and isotherm data were used to calculate the surface areas of the raw materials according to the Brunauer–Emmett–Teller (BET) method (ISO 9277:2010). Isothermal conduction calorimetry (ICC) measurements were conducted at 20 °C in a 3116-1 TAM 83 Air (TA Instruments, USA) using internal mixing procedure. The apparent density of IP samples was determined by the relation between the weight and volume of each sample, while the flexural and compressive strength were determined according to the EN196-1:2016 (EN196-1:2016). Two samples were tested per each formulation and curing age. The chemical bonding structure of IP samples was analyzed using the attenuated total reflectance (ATR)-FTIR method. Absorbance spectra were collected from 4000 to 380 cm^{-1} at a resolution of 2 cm^{-1} and 32 scans per single measurement. Three IR spectra were collected per sample and the average is reported herein.

2.3. Preparation of materials

IPs samples were synthesized following the procedure described by Ascensão *et al.* (2017). In short, it involved: (a) the preparation of the alkaline medium by homogenizing the potassium silicate (if any) and KOH 14M solutions with demineralized water at 140 rpm for 300 s in a mortar mixer (Testing Bluhm & Beuerherdt GmbH, Germany); (b) manually mixing the dried solid components in a plastic container; (c) mixing the solid and liquid components for 600 s at the same speed. After mixing, the polymeric slurries were cast into 4x4x16 cm^3 metallic molds and cured for 24 h in controlled conditions (20 $\pm$ 0.5 °C and 95 $\pm$ 1.0% relative humidity). Afterward, samples were demolded and kept in room conditions (20 $\pm$ 1.0 °C and 65 $\pm$ 5.0% relative humidity) until the time of testing. XRD samples were collected from mechanical testing, then milled, sieved and dried in low vacuum at 40 °C for 3h hours prior to testing. Replicates of F14 samples with

1 dimensions of 4x4x1 cm³ were produced and cured in sealed and non-sealed conditions,
2 and its mineralogical evolution monitored over time. Thinner samples were produced
3 with the aim of reducing the influence of sample thickness and to guarantee a
4 homogeneous (if any) CO₂ exposure and carbonation. Prior to XRD acquisition, the
5 samples were crushed in an agate mortar, then sieved ($\leq 90\mu\text{m}$) and dried in a low
6 vacuum chamber (MMM VVCell model) overnight.

7 In ICC measurements, the solid raw materials (2.0g) and the activating solution were
8 stored in the admix ampoule for a minimum period of 12h prior to the experiment to
9 minimize outside heat turbulence and allow for calorimeter stabilization. Once the
10 activating solution was injected, the slurries were mixed for 1 minute. One replicate of
11 each mixture was tested and the average values are reported here. A similar procedure
12 was used to prepare three control slurries using demineralized water. Control slurries
13 replicate the same conditions as their polymeric counterparts, both in terms of S/L and
14 solid precursor portions. Such data were used to account for the heat flow due to
15 wetting processes.

18 **2.4. Design of experiments**

19 Two experimental programs were defined to assess the impact of different synthesis
20 parameters on the reaction kinetics and their correlation with IP properties. In the first
21 experimental program, EP1, a “Two-Level-Full-Factorial” design was defined to
22 evaluate the influence of S/L ratio and K₂O/SiO₂ molar ratio on the reaction evolution
23 and IP properties. In this experimental program, only potassium hydroxide solutions
24 were used to prepare the activating solution. A second IP batch was prepared to evaluate

the impact of introducing soluble silicates into the activating solution (experimental plan 2, EP2).

The plasmastone used as the main precursor presented low Al content but significant amounts of iron and calcium. Depending on their form, calcium and iron compounds can act either as network formers or network modifiers, and have a remarkable influence on the reaction kinetics and the degree of crosslinking in the final polymeric structure. It should be mentioned that Al-Fe/Ca substitution imposes considerable changes on an IP's structure, and Fe-Si-Ca IPs are structurally different from conventional aluminosilicate geopolymers. Despite the latter consideration, Fe_2O_3 and CaO were considered in the definition of oxide molar ratios. $\text{SiO}_2/(\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3+\text{CaO})$ molar oxide ratios were fixed at 1.00, and the formulations were designed accordingly. The water content of the activating solution was adjusted to achieve the pre-defined S/L and oxide molar ratios. A full description of the two experimental programs is given in **Table 1**; dashed lines identify the compositional parameters studied.

3. Results and Discussion

3.1. ICC testing

Fig. 2a, b) show the heat evolution rate and cumulative heat evolution of the polymeric slurries where no soluble silicates were introduced into the activating solution (EP1). **Fig. 2c, d)** show the effect of potassium silicate on slurries' kinetic evolution (EP2).

The first exothermic peak (termed peak I) appeared immediately after mixing followed, in some cases, by a second smaller and broader peak (termed peak II). Peak I required less than 5 minutes to reach the maximum heat release rate in all slurries. The initial exothermic peak is often attributed to instant sorption of the activating solution at the precursors' surface and ensuing dissolution processes. The aluminosilicates' dissolution was promoted by the highly alkaline environments and, depending on synthesis parameters (e.g. precursors SSA), can occur instantly after wetting of the precursors.

The heat evolution rate was monitored over a period of 168 h and no peaks were recorded after the initial 72 h. Considerable alkali concentration and high specific surface area of the precursors promote fast nucleation of aluminosilicate gels and rapid setting of slurries, which hinder reorganization or crystallization at later stages (Zhang, 2012). These results are in agreement with previous works where it was demonstrated that high Si/Al ratios increase structural stability and reduce the formation of zeolite-like crystalline structures (Duxson, 2007).

Table 2) shows the maximum heat release of the slurries and respective control systems. The heat evolution rate of the control groups was monitored for a period of 24h. As expected, no peaks were recorded after the initial 5 minutes (not shown here in detail for the sake of brevity). The exothermic peak in the control systems can be attributed solely to wetting processes, while the difference in peak I magnitude between the slurries and their control groups can be seen to be a result of dissolution processes. Thus, slurries' kinetic data demonstrate that both physicochemical processes (wetting and dissolution) coexist in the initial reaction stage and contribute to peak I magnitude. The different magnitudes of peak I in the control groups reflect the differences in S/L ratios and solids' mixture portions.

In EP1, the heat release in the control systems increases as S/L rises, which suggests that, under the conditions tested here, the solid content is the rate-controlling factor on heat release, due to wetting processes. On the other hand, the heat release attributed to dissolution of the precursors did not present a consistent trend: $F_{11} > F_{12}$; $F_{13} < F_{14}$; $F_{11} > F_{13}$; and $F_{12} \approx F_{14}$. In low K_2O/SiO_2 ratio slurries, heat release due to dissolution processes rose as the solid content increased, but in slurries with $K_2O/SiO_2 = 0.26$, this increase was less significant.

Two distinct trends can be seen in relation to S/L ratio. At low S/L, peak I magnitude increases as alkali concentration rises. As the concentration of alkalis in the activating solutions employed rises, the potential to hydrolyze T-O (T=Al, Si) bonds in the precursors increases. Salman *et al.* (2015) suggest that the reaction kinetics may be also enhanced due to the hydrolysis of Si-O-Ca and Ca-O-Ca linkages. However, when considering slurries with $S/L = 2.50$, the increase of alkaline solution reduced peak I magnitude ($F_{11} > F_{12}$), which indicates lower immediate dissolution for the precursor. F_{12} kinetic data suggest that combining high S/L and K_2O/SiO_2 ratios reduces the activation solution activity at very early stages of the reaction. Yet, the characteristic deceleration after the initial peak was less pronounced. This demonstrates the continuous nature of the reaction and indicates the contribution to peak I of oligomerization and polymerization processes, which occur in parallel with the dissolution of silicate and aluminate units (**Fig. 2a, b**). The absence of peak II in F_{12} heat flow curves, which is commonly attributed to gelation and polymerization stages, supports the idea of such a reaction mechanism. The combined effect of increasing the content of highly reactive precursors and the alkalinity of the activating solution is to accelerate the dissolution and nucleation stages, which promotes the immediate achievement of the critical concentration necessary to start the IP network formation. As

a result, F12 peak I and II appear to overlap in the isothermal calorimetric curves, broadening the exothermic peak but reducing its maximum magnitude. The latter is corroborated by the anticipation of peak II either as the S/L increases from F13 to F11, or as K_2O/SiO_2 rises from F13 to F14, with similar trends expected for F12. It should be noted that peak I of F13 and F14 were not sharp. One possible explanation for such a phenomenon is the formation of transient products at very early stages of reaction when different physicochemical processes coexist. Such phenomena seem to be prompted by less concentrated systems but did not present a significant impact on the reaction extent after seven days (**Fig. 2b**). The cumulative heat curve shows that the amount of heat released in the early stage (initial 24h) is increased by rising solid content. However, higher K_2O/SiO_2 ratios anticipate the initial heat release. At later stages the reaction progression is mainly governed by the K_2O/SiO_2 ratio, which suggests a similar degree of precursors dissolution at a given K_2O/SiO_2 . However, when comparing F11-F13 and F12-F14, very distinct mechanical performances were observed, as will be discussed in Section 3.4. The formation of silica-rich gels is known to have a significant role in strength development (He, 2016) and the higher content of highly reactive SF in F11 and F12 may contribute to increased formation of polymeric and ordinary hydration products, thus promoting an IP's stability. Further, lowering S/L ratio results in severe crack formation, possibly due to the existence of severe drying shrinkage phenomena, further diminishing the stability of the polymeric structures. The above hindered direct correlation between the isothermal profiles of F13 and F14 and their mechanical performance.

The effect of soluble potassium silicates on reaction kinetics is shown in **Fig. 2c,d**). The introduction of potassium silicates in the activating solution exerted a considerable influence on heat flows. In F21 and F22 slurries, the second exothermic peak was

1 suppressed and the heat release associated with the precursors' immediate dissolution
2 was considerably diminished (**Table 2**). Nonetheless, the already available Si species in
3 the activating solution accelerated the gelation and polymerization stages, which
4 resulted in a single small, broad exothermic peak. K_2O/SiO_2 remains the governing
5 parameter determining the reaction extent, but distinct trends between F21 and F22
6 slurries and their silicate-free counterparts were found. The presence of silicates in the
7 activating solution is expected to increase the formation of reaction products, generating
8 higher cumulative heat release (Salman, 2015). In fact, F21 presented higher cumulative
9 heat release values than F11. In these slurries, the slight reduction of hydroxides in the
10 activating solution - implying a lower degree of precursor dissolution - was
11 compensated by the higher formation of reaction products, resulting in a slight increase
12 of the overall cumulative heat release after 7 days (**Fig. 2d**). IPs' apparent density
13 (**Table 3**) and mechanical strength results (**Fig. 5**) show densification with silicate
14 introduction, which corroborates the isothermal data. Despite similar densification and
15 increase of mechanical strength observed in both F22 and F12 samples, the cumulative
16 heat released was shown to be reduced in F22. In fact, the combined effect of a high
17 K_2O/SiO_2 ratio along with the introduction of potassium silicate in the activating
18 solution was found to considerably increase the viscosity of F22, which might have
19 affected the slurry's homogeneity during ICC experiments. Thus, F22 kinetic data are
20 not in line with the rest of the F22 characterization and, therefore, was disregarded in
21 further calorimetric analysis and discussion.

22 Finally, it should be mentioned that the reactions (both in EP1 and EP2) did not cease
23 within the testing period as the cumulative heat curves still presented positive slopes.
24 Ongoing reactions after seven days of curing can still cause minor structural
25 rearrangements and have an impact on IP strength development.

3.2. XRD analysis

Fig. 3a) shows the XRD patterns of the precursors used in these experiments. PS and SF patterns exhibited a pronounced hump between $20\text{-}40^\circ$ and $15\text{-}30^\circ 2\theta$ respectively, confirming their predominantly amorphous nature. The XRD pattern of SF presents only one crystalline peak, which has been identified as moissanite (SiC). By comparing precursors and IP patterns, it is evident that IP binders retain a mainly amorphous structure (**Fig. 3a-c**). When compared with PS patterns, no significant shifts in the hump center towards higher 2θ values were observed, as previously reported in metakaolin-based systems (Zhang, 2012). Sharp peaks appeared in the IPs' patterns, revealing the formation of new crystalline phases whose presence and intensity varies according to the synthesis conditions. **Fig. 3b)** and **c)** show the XRD patterns of IPs from EP1 and EP2 after 28 days of curing. Calcite (CaCO_3 ; PDF 01-088-1807) was identified in all patterns, while vaterite (CaCO_3 ; PDF 01-074-1867), a metastable phase of calcium carbonate, was only detected when lower S/L and no K-silicate was used (see EP1 samples F13 and F14 (**Fig. 3b**)).

Alkali activated materials are known to be prone to carbonation, which is generally attributed to two factors: i) the pore solution of high pH facilitates the capture and hydration of atmospheric CO_2 , which then reacts with calcium species to form calcium carbonate species; and ii) the carbonation of the reaction products at atmospheric conditions (Salman, 2015). In EP1, as S/L diminished the number of pores and cracks rose, which facilitated the access of atmospheric CO_2 to the pore solution and inner reaction products. Consequently, lowering the S/L ratio enhanced the formation of carbonated species and matrix carbonation. A crystallinity increase can be seen in **Fig. 3b)**. Such an increase of crystallinity promoted by lowering S/L ratios is in agreement

with previous findings (Provis, 2005) and is consistent with the ATR-FTIR observations presented in **3.3**. Furthermore, **Fig. 3e**) shows the mineralogical variation of F13 and F14 according to the probe collection location (surface and bulk samples). External surfaces, being more exposed to atmospheric CO₂, presented high-intensity crystalline peaks, whereas, in the overall sample, only low-intensity crystalline peaks were detected. Such results suggest that atmospheric CO₂ exposure prompted calcite formation, and additional experiments (XRD in samples matured in sealed conditions) were conducted to correlate such carbonated products to atmospheric carbonation and to monitor the IPs' mineralogical evolution over time. In **Fig. 3d**) samples cured in room conditions are denoted as F14_RC and the preceding number indicates the maturation age, e.g. F14_28RC corresponds to the F14 sample, cured for 28 days in room conditions. At early stages, both in sealed and non-sealed samples, only a small intensity crystalline peak was identified as calcite (CaCO₃; PDF 01-088-1807). The similarity between the XRD patterns suggests that, even during mixing, Ca²⁺ released from dissolution of the precursor reacts with atmospheric CO₂. Moreover, the slight increase of the crystalline peak intensity over time in sealed samples can be explained by the presence of trapped air, which will continually react with the available calcium species (**Fig. 3d**). After seven days, in non-sealed F14 samples (termed F14_7RC) vaterite was identified and calcite peak intensity had risen slightly. The same trend was observed at later stages, with vaterite being the only identified phase in non-sealed samples (**Fig. 3d**). These results seem to confirm CO₂ exposure as the predominant factor contributing to IPs' carbonation. However, dedicated research is needed to fully describe the carbonation mechanisms involved as no conclusive evidence is available yet.

In **Fig. 3c**) the XRD patterns of EP2 samples are shown. One can see that the introduction of soluble silicates into the activating solution has a minor impact on the formation of new crystalline phases. Similar carbonated products with comparable intensity peaks were identified in all EP2 samples, indicating similar carbonation extension. No vaterite was detected in F21 and F22 samples.

In both EP1 and EP2, the influence of the K_2O/SiO_2 was found to be minor, but a small decrease in the crystalline peaks' intensity can be seen when K_2O/SiO_2 rises. Increasing the K_2O/SiO_2 molar ratio contributed to the further densification of the IP samples and led to the formation of less porous structures (**Table 3**). Thus, by contributing to the further densification of the samples, increasing K_2O/SiO_2 may partially limit the access of atmospheric CO_2 to samples' inner regions and so contribute to limiting the formation of carbonated species. Carbonation mechanisms due to atmospheric CO_2 exposure govern IPs' carbonation extension and the eventual products formed. The results presented here demonstrate the considerable impact of S/L, where increasing K_2O/SiO_2 and introducing soluble silicate in the activating solution further reduced the formation of carbonated products. Therefore, an effective way to minimize carbonation of the samples and the formation of carbonated products may consist of maximizing IP densification through compositional and synthesis design.

Matrix and pore solution carbonation may also have a beneficial impact and enhance IPs' performance in some applications, however. Monoclinic-domatic crystals are known to have high hardness and molar volume, and by filling the porous structure they can contribute to increase an IPs' mechanical resistance and so extend its service life. With the exception of F13 and F14, the compressive strength increased in all samples during the testing period mainly due to structure consolidation (**Fig. 5**). It is worth noting, however, that the apparent density rose only in F21 and F22. In the latter, the

formation of carbonated products is able to compensate for water loss upon curing and contribute to the sample's densification. In view of the above, further research is needed to comprehend the impact of the curing atmosphere on an IP's mechanical performance and to assess the technical and economic viability of curing Fe-Si-Ca rich IPs in CO₂ rich environments.

3.3. ATR-FTIR analysis

The attenuated total reflectance ATR-FTIR method has been extensively used to characterize the chemical bonding of inorganic polymeric structures (Kriskova, 2015). Synthesis parameters affect gel development and hence determine an IP's mechanical performance. ATR-FTIR measurements were performed on samples with at least 90 days of curing; under this condition, gels were assumed to be in a near stable state.

Fig. 4a) and b) show the IR spectra of PS and the chemical bonded structures of the synthesized IPs in EP1 and EP2, respectively. The IR spectra of PS showed three main peaks that correspond to: a) the T-O (T=Al, Si) bonds stretching and bending vibrations at 471 cm⁻¹; b) Si-O bonds bending vibration at 699 cm⁻¹; and c) the asymmetric and symmetric vibration of Si-O-T bonds at 907 cm⁻¹ (Kriskova, 2015).

The presence of iron oxide phases is often denoted in IR spectra by a band at around 600-700 cm⁻¹ (Hertel, 2016); in this case it overlapped with the band corresponding to Si-O bonds' bending vibration. All IP samples presented the same peaks as the main precursor, albeit with a different shape, intensity and position. The peak at 471 cm⁻¹ shifted to lower wavenumbers and was positioned at around 434 cm⁻¹. No systematic correlation was depicted between the compositional parameters studied here and the amplitude of the shift. The peak at 907 cm⁻¹ was also relocated to higher wavenumbers, which can be attributed to the dissolution of the precursor and the formation of a new,

more Si-rich material, possibly with a greater amount of Si-units in higher coordination (Peys, 2017). When comparing the spectra of EP1 samples, lower S/L ratios can be seen to promote higher peak displacements relative to the main precursor (PS), which indicates differences during the polymerization reaction and in the final binder structure. The shift of the Si-O-T band towards higher wavenumber values indicates the formation of more Si-rich reaction products at later stages of the reaction when the S/L ratio rises. These results are in agreement with previous findings reported by Hajimohammadi *et al.* (2017). However, the introduction of soluble silicates in the activating solution did not induce further considerable changes to the position, shape or intensity of this peak, which suggests the formation of similar reaction products (**Fig. 4b**). Nonetheless, the displacement of these two peaks relative to the precursors' spectra, observed both on EP1 and EP2, confirms the reorganization of the chemical structure, which agrees with XRD measurements discussed previously. Moreover, three new peaks were formed. The broad peak between 2500 and 3700 cm^{-1} and the smaller peak at around 1645 cm^{-1} represent H₂O molecules on the IP samples, which correspond to the H-O-H bonds' deformation and the O-H groups' stretching vibrations, respectively. The different processing parameters tested have a small impact on the peak at around 1645 cm^{-1} . Yet, increasing the solid content and introducing soluble silicates in the activator narrowed the broader peak at 2500-3700 cm^{-1} and decreased its intensity, indicating a decrease of the H₂O molecules present. A small peak between 1400 and 1450 cm^{-1} appears in all IPs' spectra, and a fourth peak located between 870 and 880 cm^{-1} appeared in samples F11, F21, F13 and F14. Those peaks represent the O-C-O stretching vibrations from carbonate groups. The formation of such carbonate groups is often attributed to the reaction of free Ca cations with atmospheric CO₂ (Salman, 2015) and are in agreement

with XRD data discussed in 3.2. ATR-FTIR data corroborated that the formation of carbonated species is greatly enhanced when lowering the S/L.

3.4. Mechanical Properties

Fig. 5) shows the temporal evolution of the IPs' flexural and compressive strength and corresponding standard deviations. Despite considerable differences in heat evolution between the F11 and F12 slurries, after 7 days of curing they both presented similar compressive and flexural strength results. More intensive exothermic reactions indicated higher degrees of polymerization, binder formation and further densification but, as suggested in previous works (Ascensão, 2018), lowering the K_2O/SiO_2 molar oxide ratio may have a beneficial effect on IPs' mechanical performance. Four simultaneous effects may contribute to such behavior: (i) the lower dissolution of the precursors and subsequent gel formation result in lower shrinkage values; (ii) crack development and propagation is now limited by the presence of undissolved particles which was increased by lowering the K_2O/SiO_2 molar ratio (Machiels, 2014); (iii) a delayed effect on stiffness development (E-modulus), as higher H_2O/K_2O ratios decrease the rate of IP binder formation, resulting in lower autogenous shrinkage (Beersaerts, 2017); and (iv) less intensive exothermic reactions decrease the internal temperature during the polycondensation process, hence preventing crack formation (Machiels, 2017). In fact, F11 samples presented a higher compressive strength increase and lower flexural strength loss over time. Thus, these results show that an increase of the reaction extent and binder formation do not intrinsically increase the IPs' mechanical performance, and a certain degree of undissolved particles should be promoted in the mix design. Further, F13 and F14 samples presented very low compressive and flexural strengths even after 28 days of curing. Despite the similar

1 cumulative heat release of formulations F11-F13 and F12-F14 after 7 days, suggesting a
2 similar reaction extent, lowering the S/L ratio results in severe crack formation and
3 compromises the stability of the hardened bodies.

4 On the other hand, the introduction of soluble silicates had a positive impact on the
5 IPs' mechanical performance. As can be seen in **Table 3**, apparent density increases
6 following the introduction of soluble silicate despite there being no notable impact on
7 reaction kinetics or mineralogical composition. The consolidation of the polymeric
8 structure over time was also positively affected, resulting in higher compressive and
9 flexural strengths at later ages. It is worth mentioning, however, the minor reduction of
10 flexural strength over time in samples F11 and F12. Such results suggest that soluble
11 silicates promote more densified structures and, by doing so, contribute to the IPs'
12 increased strength development. Further, F21 and F22 presented comparable
13 mechanical properties, confirming that a certain degree of undissolved particles is
14 favorable to strength development and can compensate for less extensive reactions.
15 The large-scale application of Fe-Si-Ca IPs will be ultimately dictated by their
16 economic viability. Therefore, identifying the possibility of decreasing K_2O/SiO_2 molar
17 ratios through proper mix design while maintaining IPs' mechanical features constitutes
18 a significant insight into the development of novel waste-based products.

19 20 **4. Conclusions**

21 In the present work, kinetic and structural analysis of Fe-Si-Ca rich inorganic
22 polymeric binders (IPs) was performed and their hardened properties correlated to the
23 reaction progression. The developed IPs were synthesized using high residue content
24 (92.7 wt% of solid content) and low synthesis temperature (20°C). The resulting IPs
25 presented compressive strengths up to 119 MPa, which make them potentially viable

1 candidates for high-value applications analogous to those where Ultra-High
2 Performance Concrete is currently used. Such applications may include - among others -
3 the rehabilitation of building elements, architectural features, roads, bridges, off-shore
4 structures and vertical components such as windmills. Results showed that IPs present
5 adaptable properties that can be controlled by proper mix design. Solid-to-liquid ratio
6 was found to govern IPs' early-age reaction kinetics, whereas the K_2O/SiO_2 molar ratio
7 controlled their cumulative heat release. Notwithstanding this, lowering K_2O/SiO_2 had a
8 beneficial effect on IPs' mechanical performance when no silicate species were present
9 in the activating solution. The effect of introducing soluble silicates into the activating
10 solution was less significant on reaction kinetics but did lead to IPs with more densified
11 structures and enhanced mechanical performance.

12 Thus, by properly combining the effect of the studied parameters, IPs with low
13 alkali content were synthesized without negatively affecting their strength development.
14 These results have shown that innovative waste-based materials can be produced from
15 an as yet unexplored waste stream and contribute to the development of robust and
16 adaptive mix designs. Further, by making it possible to accommodate slags' variability,
17 it has been shown to be possible to establish resilient processes wherein Fe-Si-Ca rich
18 IP binders' properties can be tailored solely by controlling the production process. The
19 insights provided here aim to stimulate industrial symbiosis by reintegrating residues
20 from high-temperature processes in the production of construction materials and thereby
21 increase the sustainability of both sectors.

22 23 **5. Acknowledgments**

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721185. This publication reflects only the author's view, exempting the Community from any liability. Project website: <http://new-mine.eu/>

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Table Captions:

Table 1- Experimental plan- dashed lines identify the compositional parameters studied in experimental program.

Table 2- Maximum heat release of the slurries and respective control systems. The difference between initial peak magnitude of the slurries and its control groups is represented by Δ magnitude.

Table 3- IPs apparent density and corresponding standard deviations.

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1 **Table 1** – Experimental plan- dashed lines identify the compositional parameters studied in experimental program.

Experimental plan	Code	Mixture portion (wt %)					Solid/liquid wt ratio	Molar ratios	
		PS	SF	K-silicate _(aq.)	KOH _(aq.)	H ₂ O		(SiO ₂ / (Al ₂ O ₃ +Fe ₂ O ₃ +CaO))	K ₂ O/ SiO ₂
1	F11	66.3	5.2	0.0	17.5	11.0	2.50	1.00	0.20
	F12	66.3	5.2	0.0	23.0	5.6	2.50		0.26
	F13	52.4	4.1	0.0	13.9	29.6	1.30		0.20
	F14	52.4	4.1	0.0	18.2	25.4	1.30		0.26
2	F11	66.3	5.2	0.0	17.5	11.0	2.50		0.20
	F21	67.4	4.1	4.8	16.9	6.9	2.50		0.20
	F12	66.3	5.2	0.0	23.0	5.6	2.50		0.26
	F22	67.4	4.1	4.8	22.4	1.4	2.50		0.26

Table 2 - Maximum heat release of the slurries and respective control systems. The difference between initial peak magnitude of the slurries and its control groups is represented by Δ magnitude.

Experimental plan	Code	Peak I maximum mW/g	Control maximum mW/g	Δ magnitude mW/g
1	F11	13.74	3.98	9.77
	F12	9.38	3.98	5.40
	F13	4.65	0.82	3.83
	F14	7.11	0.82	6.29
2	F11	13.74	3.98	9.77
	F21	6.10	2.70	3.40
	F12	9.38	3.98	5.40
	F22	5.09	2.70	2.39

1 **Table 3** - IPs apparent density, and corresponding standard deviations.

Experimental plan	Code	Apparent density 7 th day	Apparent density 28 th day
		g/cm ³	g/cm ³
1	F11	2.20±0.01	2.18±0.01
	F12	2.34±0.02	2.31±0.06
	F13	1.62±0.01	1.39±0.02
	F14	1.71±0.03	1.55±0.01
2	F11	2.20±0.01	2.18±0.01
	F21	2.26±0.00	2.28±0.01
	F12	2.34±0.02	2.31±0.06
	F22	2.24±0.07	2.41±0.00

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Figure captions:

Fig. 1- Synthetic plasmastone particle size distribution.

Fig. 2- Isothermal calorimetry curves of IP samples: a) and c) heat evolution rate of EP1 and EP2 systems, respectively; and b) and d) cumulative heat evolved in EP1 and EP2 systems, respectively. The insert graph in a) and c) shows a chose-up of the initial heat peak (peak I). In c) and d) open symbols and dashed lines are used for identifying EP2 systems being EP1 data provided for direct comparison.

Fig. 3- XRD patterns of raw materials and IP samples: a) plasmastone and silica fume; b) and c) IP samples after 28 day of curing at room conditions, EP1 and EP2 respectively; d) F14 temporal evolution upon different curing conditions and e) mineralogical variation of F14 according sample collection (surface or bulk samples).

Fig. 4- FTIR spectrum of IP samples: a) effect of S/L and K_2O/SiO_2 molar ratio, EP1 and b) impact of soluble potassium silicate addition, EP2.

Fig. 5- IPs flexural and compressive strength temporal evolution and corresponding standard deviations.

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2 **Fig. 1-** Synthetic plasmastone particle size distribution.

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Fig. 2- Isothermal calorimetry curves of IP samples: a) and c) heat evolution rate of EP1 and EP2 systems, respectively; and b) and d) cumulative heat evolved in EP1 and EP2 systems, respectively. The insert graph in a) and c) shows a close-up of the initial heat peak (peak I). In c) and d) open symbols and dashed lines are used for identifying EP2 systems being EP1 data provided for direct comparison.

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2 **Fig. 3-** XRD patterns of raw materials and IP samples: a) plasmastone and silica fume; b) and c) IP samples after 28 day of curing at room
3 conditions, EP1 and EP2 respectively; d) F14 temporal evolution upon different curing conditions and e) mineralogical variation of F14
4 according sample collection (surface or bulk samples).

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3 **Fig. 4-** FTIR spectrum of IP samples: a) effect of S/L and K₂O/SiO₂ molar ratio, EP1
4 and b) impact of soluble potassium silicate addition, EP2.

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Fig. 5- IPs flexural and compressive strength temporal evolution and corresponding standard deviations.