

RECYCLING OF IRON-RICH INORGANIC POLYMERS

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Introduction

Inorganic polymers (IP) can be formed *via* a reaction between (iron)aluminosilicate precursors and alkalis, most often K-, Na- silicates¹. In a number of cases, the precursors are highly amorphous industrial residues, either from metallurgical or from energy production processes, whereas more recently, also residues from municipal solid waste incineration/vitrification processes are being investigated. Due to their relatively low carbon emissions, IP represent a greener alternative to Portland cements². However, prior to granting IP a green label, other significant environmental impacts should be investigated. One of the important aspects of the sustainability is their end-of-life impact³. This becomes even more important in the view of latest research, that has proven the generation of construction demolition waste increases. It is therefore the aim of this work is to investigate whether the waste of iron, silicate-rich IP could be incorporated as a precursor in a new matrix and to contribute to the topic that relates to IP's sustainability.

Materials and Methods

Finely-milled water granulated fayalite slag from secondary copper production was used in this work. The chemical composition was determined by means of X-ray fluorescence spectroscopy (XRF, Philips PW 2400). The mineralogical analysis was performed by means of X-ray diffraction analysis (XRD, Bruker D2 Phaser) using CuK α radiation of 30 kV and 10 mA. 10 wt% of analytical grade crystalline Al₂O₃ was added to the slag and homogenised in an ethanol suspension for 5 minutes (McCrone, Micronizing mill). The X-ray patterns were collected with step size of 0.02° 2 θ and step time of 0.6 seconds per step. The qualitative and quantitative analyses of the XRD patterns were performed using the EVA and TOPAS academic software, respectively.

The IP was prepared by activating the slag with a potassium silicate solution (1.6 SiO₂/K₂O molar ratio and H₂O of 58.8 wt%), with the slag/solution mass ratio (S/L) equal to 3.67. This IP (OIP) was cured at room temperature (RT, 21°C \pm 1°C) for 28 days and then dried at 105°C for 2 days. Subsequently, the IP was crushed with a disk mill (Fritch, Pulverisette 13) and milled in an attritor mill (Wiener 1S) for 1 hour. The milled IP was then used to synthesised five types of samples, varying the IP content, Table 1; the numeral at the beginning of each composition suggests content in wt% of recycled IP. Due to the slightly different fineness of OIP powder and/or its behaviour in an

alkaline environment, the S/L ratio was gradually adjusted in each sample to assure a similar workability of all fresh pastes, Table 1. The synthesised materials were cast in rectangular moulds $2 \times 2 \times 8 \text{ cm}^3$ and cured at room temperature (RT) until testing, at 3, 7 and 28 days.

Pulverised and freeze dried samples, cured for 28 days at RT, were subjected to thermogravimetric analysis (TGA, SDT Q600) by heating up to 1000°C with a 10°C/min rate in Ar atmosphere. Fourier Transform Infrared (FTIR) spectroscopy was performed on samples cured for 28 days, employing a platinum ATR QuickSnap™ module in an Alpha-P spectrometer (Bruker). The mechanical strength measurements were performed after 3, 7 and 28 days of curing, using a 250 kN load cell (Instron 5985) with a loading rate of 1 mm/min. Results are indicative, as only two samples per mixture were tested; the average data are presented.

Table 1: Mix design for IP samples (in wt%; S/L in mass ratio)

Sample name	Recycled IP	Fayalite slag	S/L
0IP	0	100	3.7
20IP	20	80	3.6
50IP	50	50	3.4
80IP	80	20	3.3
100IP	100	0	3.2

Results and Discussion

The chemical composition of the fayalite slag is listed in Table 2. The slag consisted of an amorphous phase (76 wt%) and fayalite (19 wt%), the rest being hercynite, magnetite and traces of other minerals. The milled slag had a D₁₀ and D₉₀ of 0.25 µm and 20.1 µm, respectively.

Table 2: Chemical composition of the as-received slag, in wt%

FeO	SiO ₂	Al ₂ O ₃	ZnO	MgO	Others
41	39	8	6	3	3

In the TGA results, Figure 1a, a double peak below 200°C was present in all cases. This peak is typically associated with the evaporation of free water and the decomposition of hydrates (peak at higher temperature). The relative intensities of the 2 peaks changed, as a function of the recycled IP present, and the second peak became more dominant as the amount of recycled material increased. This evolution indicates that more interstitial rather than free water was present in the samples with recycled IP.

The FTIR spectra of the samples are shown in Figure 1b. In all cases, the bands associated with the Si-O stretching, bending and rocking vibrations were present, but

the attention is paid to the stretching ones ($800 - 1100\text{ cm}^{-1}$) only. In all studied samples, three bands, positioned at 945 , 860 and 830 cm^{-1} , were visible. In the as-received slag, the band at about 860 cm^{-1} was the most intensive, but reached similar intensity to the one at 945 cm^{-1} in the 0IP sample. As the amount of recycled IP increased, the band at 945 cm^{-1} became more dominant, which could be attributed to the formation of the IP binder⁴. The above is in good agreement with the TGA data.

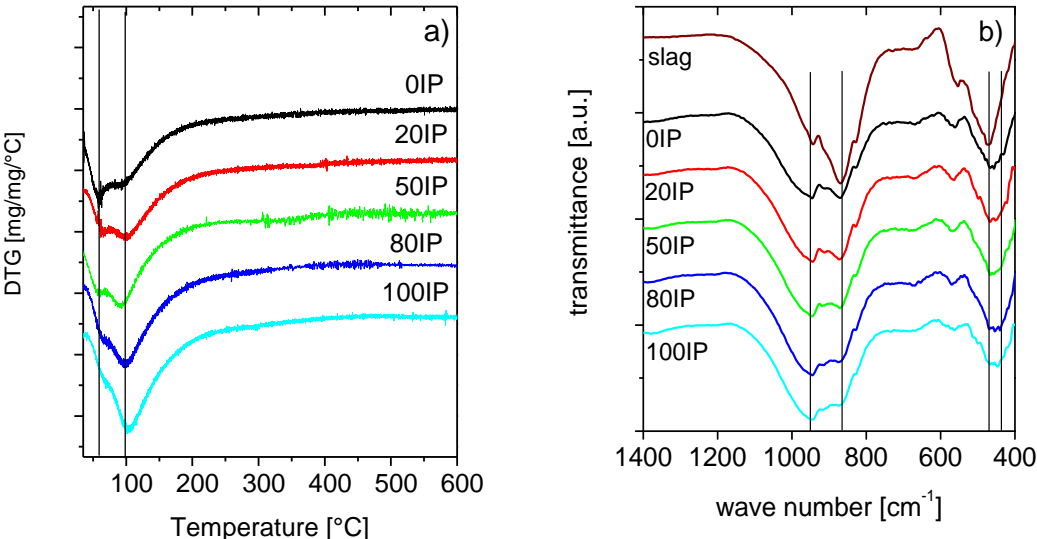


Figure 1: (a) DTG at 28 days and (b) FTIR results at 28 days

The compressive strength results are presented in Table 3, where 0IP sample is added as a reference. The mechanical strength of the samples with recycled IP incorporated was lower compared to the 0IP sample at every age, and it decreased gradually as the amount of recycled IP increased. The 28th day strength of the sample with 20 wt% recycled IP (20IP) reached 95% of the original 0IP strength, while it dropped to 78% in the 50IP sample and to 48% in the sample fully synthesised from the recycled IP (100IP). Interestingly, the process of the strength development itself was influenced by the amount of incorporated recycled IP. While the 3 day strength of the original 0IP sample reached 76% of its final strength, it only reached 67% and 62% in the 20IP and 50IP sample, respectively. The sample consisting fully of the recycled IP gained only 33% of its final strength within the first 3 days of reaction. Similar trend can be seen after 7 days of reaction. This observation suggests more sluggish kinetics as the recycled content rises, yet, it also clearly indicates that the recycled IP is still a reactive fraction in the IP synthesis.

Table 3: Compressive strength of the original and recycled IP

	OIP	20IP	50IP	80IP	100IP
3 days (3d)	32 ± 4	26 ± 3	20 ± 3	11 ± 2	7 ± 2
7 days (7d)	35 ± 3	32 ± 5	24 ± 2	17 ± 3	11 ± 2
28 days (28d)	42 ± 4	39 ± 5	32 ± 6	23 ± 5	20 ± 3

Conclusions

In the work herein, it was demonstrated that “end-of-life” inorganic polymer could be incorporated in new formulations, contributing to the synthesis of a new inorganic polymer matrix. The inorganic polymers with recycled IP have microstructural differences and mechanical strength evolution with different kinetics and ultimate values compared to the reference materials. Nonetheless, the IP that was synthesised solely from recycled IP had approximately 50% of the mechanical strength of the reference sample at 28 days, which might still be adequate for certain applications.

References

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