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THE IMPACT OF CURING CONDITIONS ON HEAVY METAL IMMOBILISATION OF Fe-RICH INORGANIC POLYMERS

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Introduction

Inorganic polymers (IP), produced through the alkaline activation of alumina-silicate rich materials, have been proposed as a sustainable alternative to Ordinary Portland Cement, which is responsible for 8 % of the anthropogenic CO₂-emission.¹ In this paper iron-silicates with low alumina content, as precursor for inorganic polymers (IP), are investigated. These iron rich silicates are obtained by plasma gasification of highly calorific waste materials, such as refuse derived fuel produced from municipal solid waste. This residue is amorphous due to water quenching and will be referred to as glass in this paper. The glasses produced through this process can contain considerable amounts of heavy metals, coming from the solid waste.

In order to get a deeper understanding of the heavy metal leaching behavior in inorganic polymers (IP's), a glass containing considerable amounts of heavy metals was used as precursor. Inorganic polymers produced were subjected to four different leaching tests. Ground glasses and IP's produced from the glasses were submerged in a nitric acid solution of pH 4 and 7 and at natural pH that stabilized between pH 10.5 and 12.5. Monolithic samples were only tested at natural pH. The influence of hydrothermal curing, namely the pressure and the temperature in the autoclave, was intensively studied.

Materials and methods

A Fe-rich glass (HM) of approximate chemical composition 37 wt.% SiO₂, 30 wt.% FeO, 13 wt.% CaO, 8 wt.% Al₂O₃ and 1 wt.% of oxides of Cu, Cr, Ni, Pb and Zn was synthesized. A second glass of similar chemistry but without addition of heavy metals' oxides was also produced for comparison (RA). The premixed metal oxide

powders were melted in a bottom loading furnace at 1450 °C for 30 minutes in a platinum crucible under Ar-air atmosphere. The melt was quenched in water to obtain a glassy material with limited crystalline precipitation. To assess whether the desired > 90 wt.% glass content was obtained after melting and water quenching, quantitative X-ray powder diffraction analysis (QXRPD, D500, Siemens) was used. Quantification was performed according to the Rietveld method using the “Topas® Academic” software.

The quenched glass was crushed in a mortar until a grain size < 5 mm. Further grain size reduction was done in a ball mill and two batches with an average grain size (d_{50}) of 20 μm and 5 μm were produced. IP mortars and pastes were prepared using a process developed in a previous work.³ IP samples were prepared from 60 wt.% of a fraction of d_{50} 20 μm and 40 wt.% of a fraction of d_{50} 5 μm , to obtain an optimal particle packing. As activating solution, a sodium-silicate solution composed of 13.3 wt.% SiO_2 , 15.6 wt.% Na_2O , and 71.1 wt.% H_2O was used. After mixing for 1 minute the activating solution with the glass, respecting a solution/glass ratio of 0.45, the standard norm sand (DIN-EN 196-1) was added using a glass/sand mass ratio of 1/3. After another minute of mixing, the mortars were pressed in a cylindrical mold at 30 MPa.

Samples were cured at four different curing conditions. At room temperature (HM20) the samples were wrapped in plastic foil for seven days and were then further cured in open air. For curing at 60 °C (HM60) samples were placed in a plastic container, which was then hermetically sealed and placed in an oven for 24 hours. Afterwards, they were cured at room temperature for six days, still wrapped in foil. The last two batches of samples were cured at 120 °C (HM120) and 180 °C (HM180) in a stainless steel pressure vessel for 24 hours. The pressure was estimated to be around 10 bar.

Table 1: Processing and curing conditions of inorganic polymer samples

Sample	solution/glass	glass/sand	curing conditions
HM20	0.45	1/3	28 days at 20 °C
HM60	0.45	1/3	24 hours at 60 °C + 27 days at 20 °C
HM120	0.45	1/3	24 hours at 120 °C + 27 days at 20 °C
HM180	0.45	1/3	24hours at 180 °C + 27 days at 20 °C

Leaching tests

Leaching tests were performed on the glass fractions and IP milled to < 80 μm . A BET surface test was performed on the crushed inorganic polymer samples to compare the specific surface of the samples. The values of the free surface shown in Table 2

are quite similar to each other, so leaching results reflect changes in the binder itself and not physical encapsulation of the metals.

Table 2: BET surface in m²/g of crushed samples used for the 24 h and the pH 4 - pH 7 leaching test

	HM20	HM60	HM120	HM180
BET surface [m ² /g]	7.81	8.75	6.85	8.09

To investigate the leaching behavior of the different heavy metals, 3 types of leaching experiments were performed:

- batch leaching test, 24 h leaching at natural pH, according to procedure CMA/2/II/A.12.¹ The particle size of the materials was very fine (< 80 µm) but still meeting the requirement of < 10 mm in the standard; this was done in order to be able to compare the leaching values of this test with the availability test.
- availability test, executed following the CMA/2/II/A.9.3² procedure. This test includes a 3 hours batch leaching test at pH 7, followed by 3 hours leaching at pH 4. The pH is kept constant by adding nitric acid. ICP-OES (Varian 720 ES) analysis was used to analyze Cu, Cr, Ni, Pb and Zn in the leachates.
- a monolithic leaching test was performed on monolith samples of approximately 30 g that were submerged in 200 ml water for 7 days.

Results

Glass characterisation and properties of the inorganic polymers

The final composition is close to the one aimed for but small deviations do exist (Table 3). For example, the amount of PbO is lower than the 1 wt.%, probably because of evaporation that starts around 950 °C.⁵ The glass fraction is around 93 wt.%. Because of the relatively oxidative character of the Ar-air atmosphere, a notable amount of magnetite was formed. Also small fractions of quartz, periclase and calcite were present.

Table 3: XRF analysis of the glasses

Wt.%	SiO ₂	FeO	CaO	Al ₂ O ₃	MnO	K ₂ O	MgO	TiO ₂	Na ₂ O	ZnO	CuO	Cr ₂ O ₃	PbO	NiO
HM	36.2	29.2	12.4	8.2	1.7	0.6	2.2	1.0	1.1	1.2	1.2	1.6	0.6	1.5
RA	38.2	30.4	14.0	8.5	1.8	1.2	1.8	1.0	0.5	bdl	1.0	0.4	bdl	bdl

bdl = below detection limit

The results for the inorganic polymers are listed in Table 4. The difference between the most dense and most porous sample is 2.2 % and a decreasing trend in apparent

porosity with increasing curing temperature can be deduced. The influence of curing conditions on the uniaxial compressive strength was substantial. After 28 days of curing at room temperature, the strength is comparable to CEMI 52.5 R mortars. The strength doubled to a value of 138 MPa when cured at high pressure for 1 day.

Table 4: Apparent porosity and compressive strength at 28 days

	Apparent porosity (vol.%)	Compressive strength (MPa)
HM20	11.9	65 ± 3.2
HM60	12.1	106 ± 6.6
HM120	10.9	119 ± 3.7
HM180	9.9	138 ± 2.8

Leaching tests

The natural pH of the leaching fluid after the 24 h and the 7 days monolithic leaching test is shown in Table 5. In both cases a pH decrease with increased curing temperatures was observed.

Table 5: Natural pH after the 24 h leaching test and after the 7 days monolithic leaching test

	pH after 24 h	pH after 7 days
HM20	11.97	12.25
HM60	11.92	12.23
HM120	11.40	10.97
HM180	11.00	10.60

Figure 1a shows that for Ni, Pb and Zn the leaching values for all IP were far below the VLAREMA limits and even had the same magnitude as the values of the glasses. The Cu and Cr values were higher than those of the glasses and the inorganic polymers need high pressure curing to meet the VLAREMA requirements. At pH 7, samples cured at room temperature leached more, with Ni being the most sensitive to this pH decrease. At pH 4 the level of Cu, Ni and Zn in the leaching fluid was very high, but also here the high pressure curing of the inorganic polymer had a pronounced positive influence. Remarkable is the fact that the Cr and Pb values were still in the same order of magnitude as the glasses. The results of the monolith leaching test in Figure 1e were very similar to the results of the 24 h leaching test in Figure 1f. This was expected because both tests were performed at natural pH. The release of heavy metals from the monoliths was slightly lower, due to a lower free surface.

The SEM-BSE images (Figure 2) partly explain why high pressure curing had a large positive effect on all the measured properties. When comparing a room-T cured sample (Fig 2a) with a sample cured at high pressure (Fig 2b), the extent of cracks' formation is very high in the first case unlike the second. Most likely, due to a better dissolution of the glass and a faster/more extended polycondensation of the inorganic polymer gel in the steam saturated environment at 180 °C, drying and shrinkage cracks like in HM20 do not form. The better dissolution of the glass also causes a higher Al_2O_3 content in the inorganic polymer gel, which lowers the Na/Al ratio, bringing it closer to 1. A Na/Al ratio of 1 delivers the best properties according to Duxson et. al.⁴ because the charge balance between the $\text{Si}^{4+} \Leftrightarrow \text{Al}^{3+} + \text{Na}^+$ ions in the alumino-silicate chain is stoichiometric. Still, a number of other reasons also determine the final outcome, the role of water in the IP structure, the role of Fe and the formation of zeolite-type phases, to name just few. The work is on-going and a more extended discussion will be presented elsewhere.

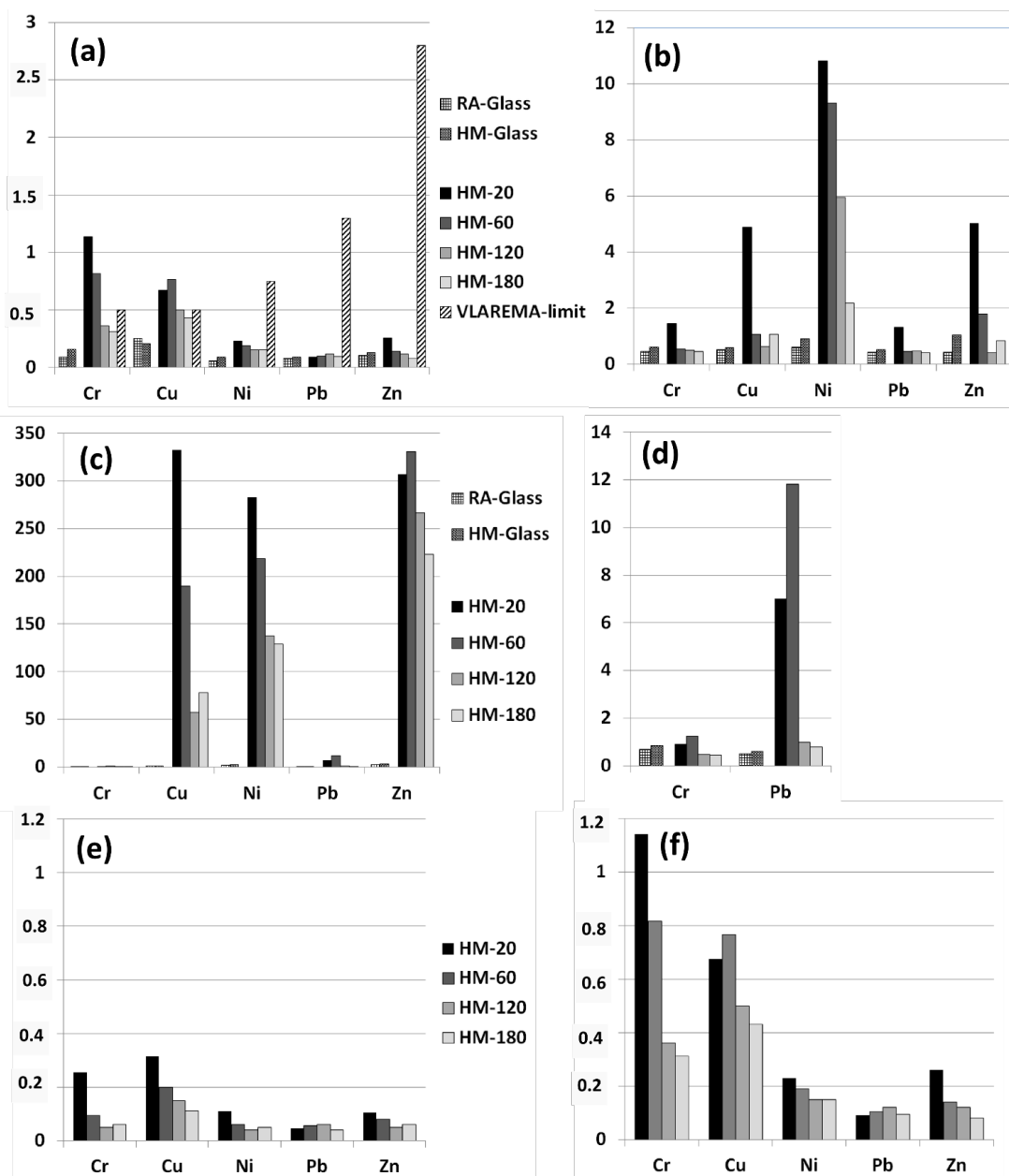


Figure 1: Leaching results in mg/(kg.dm) of: **(a)** 24 h leaching test at natural pH compared with the VLAREMA limit, **(b)** pH 7 leaching test, **(c)** pH 4 leaching test, **(d)** pH 4 leaching test: zoomed in on Cr and Pb, **(e)** monolithic leaching test at natural pH, **(f)** 24 h leaching test at natural pH at same scale as the monolithic test.

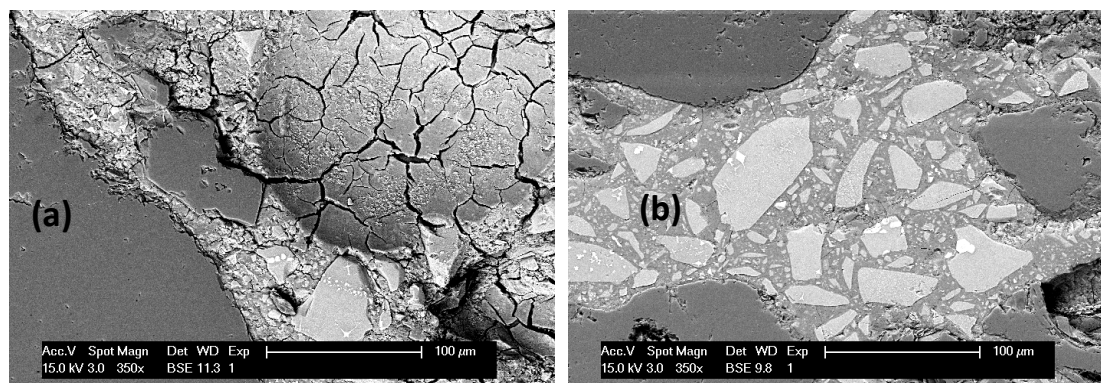


Figure 2: SEM-BSE images of polished sections of samples: **(a)** HM20 with a lot of cracks, **(b)** HM180 without cracks

Conclusion

Hydrothermal curing had a strong and positive influence on the strength, porosity and the leaching behavior of Fe-rich inorganic polymers. The overall best sample produced had a liquid/glass ratio of 0.45 and was cured for 24 hours at 180 °C and approximately 10 bar. The results are promising because this sample has an apparent porosity of 10 % and delivers a compressive strength of about 140 MPa, which is higher than most inorganic polymers reported in literature and most types of commercially available concrete. With respect to leaching, Cu, Ni and Zn are much more sensitive to a decrease in pH than Cr and Pb. Still, even with increased heavy metal content, the leaching values of all metals are below the VLAREMA standards for a 24 hours leaching test at natural pH.

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