EFFECT OF THE ACTIVATING SOLUTION’S CHEMISTRY AND VOLUME, ON THE PROCESSING AND PROPERTIES OF Fe-Si-Ca-RICH INORGANIC POLYMERS

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Introduction

In today’s concrete industry a lot of industrial by-products are already incorporated in cementitious systems as reactive cement replacer, inert filler or aggregate. Silica fume additions can increase the strength of the concrete, ground granulated blast furnace slag can have a beneficial impact on durability, whereas fly ash from coal combustion can decrease the cost and the environmental footprint. On the other hand, Fe-rich slags from the non-ferrous metal industry are currently only used as aggregates when it comes to concrete. In an attempt to up-cycle these streams, inorganic polymers (IP) come into the picture. Machiels et al.¹ and Kriskova et al.² presented the potential of Fe-silicate glasses, coming from landfill mining residues, as precursor for IP. Hertel et al.³, Onisei et al.⁴ and Iacobescu et al.⁵ demonstrated the possibility to make IP from semi-crystalline Fe-rich slags. This paper investigates the influence of the molar SiO₂/Na₂O ratio of the activating solution and of the liquid/solid (L/S) ratio, on the processing and early age properties of Fe-rich inorganic polymers.

Experimental

A synthetic glass with a chemistry similar to a Fe-rich slag of the non-ferrous metal industry, (in wt%) 50 FeO, 36 SiO₂, 12 CaO, 5 Al₂O₃ and 3 MgO, was used as IP precursor. The glass was milled to a Blaine surface of approx. 4000 cm²/g and was then mixed with the alkaline activator. The sodium-silicate activating solutions employed had 65 wt% H₂O and a varying SiO₂/Na₂O molar ratio of 1.6, 1.8 and 2.0. The latter (liquid: L) were mixed with the precursor (solid: S), respecting a L/S ratio of 0.4 and 0.5. Samples’ naming is after the molar and L/S ratio used, for example 2.0/0.5 stands for SiO₂/Na₂O molar ratio of 2.0 and L/S ratio of 0.5. The setting time and heat evolution of IP pastes were measured with Vicat needle penetration and isothermal calorimetry, using an admix ampoule, respectively. The slag powder and activating solution were first given 4 hours to equilibrate inside the calorimeter chamber and were then mixed for 1 minute in the ampoule. Compressive and flexural strength were
measured on mortars, made with 550 g of glass, 1350 g of CEN-sand, and SiO$_2$/Na$_2$O and L/S ratios as described above, at 3, 7 and 28 days, after curing at ambient temperature in closed plastic boxes. The flowability of these mortars was tested according to the EN 1015-3.

Results and Discussion

A strong increase in flowability is observed when the L/S is increased from 0.4 to 0.5 with a maximum flow of 181 mm for mortar 2.0/0.5. At a L/S ratio of 0.4, the flow is slightly decreased when the molar ratio is increased while at a L/S ratio of 0.5, the flow is increased when the molar ratio is increased.

The setting time of the mortars with molar ratio 1.6 and 1.8 is comparable, that is 4 hours for a L/S of 0.4 and 6 hours for a L/S ratio of 0.5. A drastic increase in setting to 15 hours is observed when ratio 2.0 is used. This delay is probably caused by many mechanisms acting at the same time. The decreasing pH when going from ratio 1.6 to 2.0 decreases the reactivity of the activating solution, which leads to a slower glass dissolution. It is known that increasing the alkali content of the activating solution promotes silica dissolution$^6$, and as the water content is constant in the solution, the alkali content increases with decreasing molar ratios. Another reason is that increasing the SiO$_2$/Na$_2$O decreases the amount of monomers in the solution which are assisting the dissolution. Larger and higher order silica species either potentially hinder the reaction mixture or remain unreacted. Lowering the L/S also decreases the setting time. Possible reasons for this could be the higher concentration of nucleation sites for the reactions to start, in conjunction with the fact that 20% less solid material has to dissolve to reach the critical concentration in the solution for the IP network to start forming. Mixing drier mortars also results in higher shear forces in the fresh mortar, which liberate more reactive surface by breaking the particles agglomerates. This creates a better wetting of the glass particles which also increases the speed of the dissolution and polymerisation.

Figure 1: (a) EN 1015-3 slump test results of the 6 different mortars and (b) the Vicat needle penetration test results on the 6 IP pastes
The setting time results (Figure 1b) and the calorimetry results (Figure 2a) suggest that setting and heat evolution are in practice coinciding. A minor difference in indicated kinetics is probably caused by the less intensive mixing in the ampoule and the constant temperature during the calorimetry measurement. The volume in the Vicat apparatus is 100 times higher, so an autocatalytic effect could take place due to the increased temperature caused by the heat of the reaction. When lower molar ratios are used, the height of the heat peaks is lowered and they become wider, suggesting slower dissolution. The L/S ratio does not have a significant influence on the rate of heat flow and the cumulative heat flow per mass of binder. Results expressed per mass of slag, reveal that more heat is produced for higher L/S ratio, which is related to the higher amount of slag dissolution needed before an IP network of certain rigidity starts forming. Another interesting conclusion is that for samples 0.5/1.6 and 0.5/2.0 (Figure 2c), about 23 and 28% of the heat is produced between day 7 and 28, indicating that the reactions are still on-going. This observation could explain the fact that the respective mortars gain approx. 25 and 40% of their compressive strength between day 7 and 28, a possible indication of continuous polymerisation and further cross linking of the IP. With respect to the impact of L/S ration on compressive and flexural strength, results suggest a significant decrease when it increases, for all curing times tested. The trend visible at 7 days, where an increase in the molar ratio decreases the strength, is not present anymore at 28 days and results vary per case.

Figure 2: Isothermal calorimetry results expressed per gram of paste: (a) rate of heat flow and (b) cumulative heat flow results measured on the 6 pastes for 44 hours. (c) 28 days cumulative and rate of heat flow results of paste 0.5/1.6 and 0.5/2.0
Conclusions

From an engineering perspective, the data presented herein indicate a processing window where the development of the binder is improved, by achieving a balance between workability, setting time and strength development. The strongest sample was produced with a molar SiO₂/Na₂O ratio of 2.0 and a L/S of 0.4, had a slump flow of 103 mm, a setting time around 16 hours, and delivered a compressive strength of 22 MPa at 3 days and 86 MPa at 28 days.

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References