

ON THE FOAMING KINETICS FOR THE SYNTHESIS OF POROUS INORGANIC POLYMERS

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Introduction

Inorganic polymers (IP) are relatively new materials that could replace cement-based materials.¹ They are usually formed by a reaction between a precursor and an alkali solution. A large number of by-products created during the production and recycling of metals as well as the vitrification of landfilled wastes are suitable precursors.² Replacing cement with these industrial by-products reduces the CO₂ emission and raw material consumption.³

Lightweight IP's, synthesised either by mechanical or by chemical foaming, find their application in insulation materials among others.⁴ Chemical foaming uses foaming agents such as Al, H₂O₂ or Si that react inside the fresh paste and generate gas. An example for such a reaction is given in Equation (1). The generated gas is entrapped in the IP paste resulting in a porous material.⁵



Various parameters influence the reaction kinetics of a foam. In this work, three of these parameters were investigated: a) the Si₂O/Na₂O molar ratio of the activating solution; b) the process temperature and c) the addition time of the foaming agent.

Materials and Methods

Fayalite slag from a secondary copper production, with a D₅₀ of 2.5 µm, was used as precursor consisting of 76 wt% of amorphous phase. It contained approximately 85 wt% of Fe, Si and Al, rest being Zn, Mg and other trace elements. The activating solutions were prepared by mixing Na-silicate (ABCR, 39-40% silicates in water), demi-water and NaOH pellets (EMSURE, 99-100%) until full dissolution was reached. The solutions varied in Si₂O/Na₂O molar ratio (1.0, 1.2 or 1.4) but all contained 75 wt% of water. Fine metallic Al (99.9%, AEE) powder with a particle size of 1-5 µm, was used as foaming agent. SB-2, a commercial surfactant from Sika, was added to the IP paste to improve the foam structure as well as its stability.

The reaction heat of different paste mixtures was determined by isothermal conduction calorimetry (TAM Air, TA Instruments) at 10, 20 and 40°C using an admix

ampule, which allowed the reaction to start after stabilisation of the calorimeter. The mixtures were produced using a S/L ratio of 3.33 and 0.2 wt% of foaming agent was added. For the experiments, no surfactants were added.

Foamed IP were prepared by mixing the slag with the various activating solutions (S/L ratio = 0.35), surfactant (0.02 ml/100 g slag) and Al powder. The mixing time depended on the addition time of the foaming agent. For an addition time of 5 minutes the paste was continuously mixed for 5 minutes (Bosch MFQ4070). For the addition time of 30 minutes the paste was mixed for 5 minutes and subsequently, every 4 minutes it was mixed for 1 minute (time: 9', 14', 19', 24' and 29') to ensure a homogenous paste. The samples were foamed inside a thermostatic bath to control the temperature (10, 20 or 40°C) at which the foaming took place. The height of the foams was recorded with a camera to investigate the kinetics.

Samples names are written in A-B-C-D style to clearly show the combination of parameters used, with A) activating solution, B) temperature, C) foaming agent and D) addition time. Example: 12-20-Al-5 is a sample made using an activating solution with a $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 1.2 that was foamed at 20°C with Al added after 5 minutes of mixing.

Results and Discussion

Heat of reaction

Addition of the foaming agent led to higher overall recorded heat, which is the sum of heat generated from reaction (1) and the synthesis of the IP. It is noticeable that there was only one peak visible, when Al was present, while the synthesis of the IP consisted of 2 clear peaks separated by a weaker peak as shown in Figure 1a. The first peak indicated an immediate start of the synthesis with wetting and dissolution of the slag, followed by the weaker peak until the paste reached oversaturation. This initiated the polymerisation as indicated by the second clear peak.⁶ The occurrence of one peak can be explained by the fact that the heat generated from reaction (1) accelerated the synthesis, which was finished within one hour, while the synthesis when pure slag was used concluded between 2 and 40 hours, depending on the temperature. Despite this accelerated synthesis, the temperature effect remained visible as shown in Figure 1b. An increased temperature resulted in an accelerated synthesis and increased cumulative (CML) heat flow (represented by the empty symbols), indicating that temperature influenced both the speed and amount of IP synthesis. This statement is in good agreement with the fact that the rate of dissolution is influenced by diffusion, which strongly depends on temperature. Chithiraputhiran and Neithalath reached a similar conclusion when studying fly ash based IP.⁷

The effect of $\text{SiO}_2/\text{Na}_2\text{O}$ ratio on the reaction kinetics after Al addition was also visible. However, the acceleration with decreasing $\text{SiO}_2/\text{Na}_2\text{O}$ ratio was less pronounced compared to the acceleration with increasing temperature.

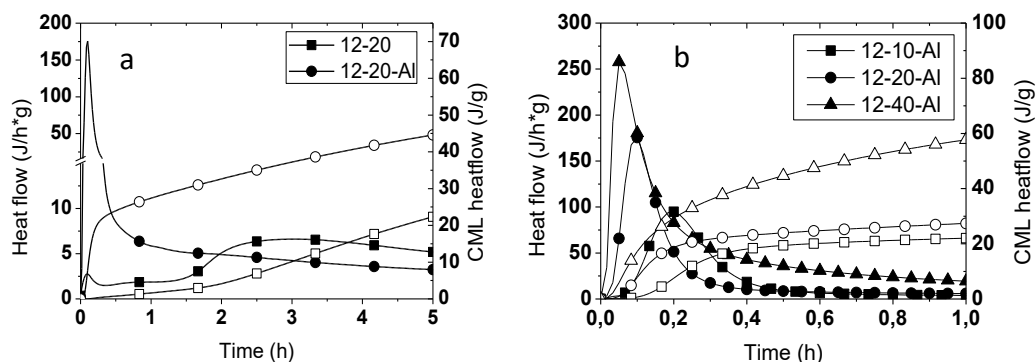


Figure 1: a) Influence of foaming agent on the polymerisation reaction. b) Influence of the temperature on the heat flow generated by the polymerisation of fayalite slag, with Al as foaming agent

Kinetics of pore formation

The influence of various parameters on the foaming kinetics is shown in Figure 2. Increasing the addition time of the foaming agent resulted in a slower foaming speed. This phenomenon can be explained by increased consumption of OH^- during longer lasting polymerisation,⁸ resulting in the reduction of the foaming agent reactivity, as listed in Equation (1). It was also observed that foams with Al addition after 5 minutes of mixing, were more likely to collapse compared to the foams with Al addition after 30 minutes. Postponing the foaming gave the precursor more time to dissolve, resulting in a higher level of polymerisation, which leads to an increased connectivity of the gel network and stabilisation of the foam.

The $\text{SiO}_2/\text{Na}_2\text{O}$ ratio influenced the time at which the paste started foaming and the final height of the foam, but not the foaming speed itself. A decreased $\text{SiO}_2/\text{Na}_2\text{O}$ ratio resulted in earlier foaming and a reduced foaming height. The former could be explained by the increased amount of OH^- in the paste which increased the reactivity of the foaming agent. The latter was probably caused by the faster setting of pastes containing a decreased $\text{SiO}_2/\text{Na}_2\text{O}$ ratio, which lead to hardening before the foaming was completed.

It appears that the increased temperature resulted in an earlier and faster foaming. Similar results were also found by Henon *et al.* who concluded that the temperature influenced the kinetics of foaming.⁹

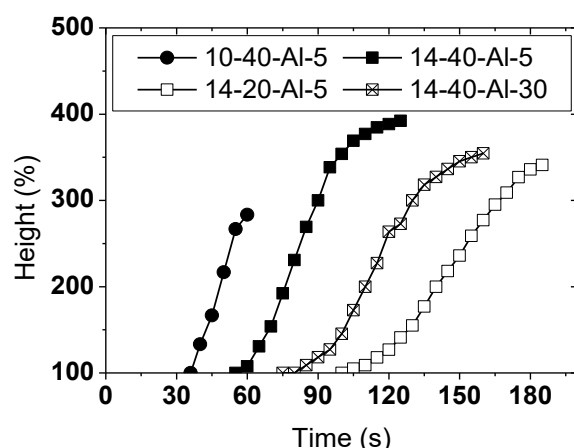


Figure 2: Influence of the various parameters on the foaming kinetics

Conclusions

Lightweight IP were synthesised by alkali activation of fayalite slag with Al powder. The influence of various parameters such as $\text{SiO}_2/\text{Na}_2\text{O}$ ratio, temperature and addition time of the foaming agent on the kinetics were investigated. The temperature and $\text{SiO}_2/\text{Na}_2\text{O}$ ratio mainly influenced the height (total volume) and speed of the foaming while the addition time played an important role in the stability of foams. Maximum foaming was obtained at 40 °C using an activating solution with a $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 1.4 and by adding the Al-powder after 5 minutes of mixing.

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