

Towards Sustainable Inorganic Polymers: Production and Use of Alternative Activator †

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Abstract: Inorganic polymers are considered to have a much smaller CO₂ footprint than traditional Portland cements. The possible environmental impact reduction was calculated to be up to 77% of a CEMI ordinary Portland cement (OPC)-based mortar, while the CO₂ emissions were reduced by up to 83%. The highest contribution to the total CO₂ footprint of inorganic polymers is related to the manufacturing of alkali activators. Within this context, the current work discusses the synthesis of inorganic polymers made from Fe-rich precursor and alternative silicate solutions. The obtained results indicate that there is no significant difference between an inorganic polymer prepared from alternative and commercially available solutions, which confirms that the waste glass can be used as alternative raw material in the production of sodium silicate.

Keywords: inorganic polymers; alkali activators; alternative raw material



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1. Introduction

Two main drivers of the enormous attention recently paid to inorganic polymers (IP) are (i) the possibility to incorporate industrial by-products as raw materials and (ii) the low(er) carbon dioxide (CO₂) emissions compared to OPC. Analysis undertaken to calculate the CO₂ emissions showed that the IP pastes typically have a range of emissions between 100–800 kg, whereas the CO₂/t, depending on the mixture used [1]. Compared to a Portland cement-based system, the CO₂ emissions of an IP synthesized from, e.g., Fe-rich residue, can be reduced by up to 83% [2]. Yet, the highest CO₂ emissions associated with these alkali-based binders are related to the alkali activator itself [3]. More specifically, e.g., to sodium silicate, whose total CO₂ emission can be as high as 570 kg CO₂/t [4]. Therefore, research has been focused on exploring the use of alternative raw materials that can be used as alkali activators. Peys et al. [5] used biomass ashes as an alkaline activator in the synthesis of metakaolin-based inorganic polymers. They blended two families of biomass ashes with (meta)kaolin in various proportions and water. The cured pressed mortars reached up to 40 MPa compressive strength. Puertas and Carrasco [6] used urban and industrial glass waste as a potential alkaline activator for (ground granulated) blast furnace slag and concluded that silicon from glass waste dissolved in NaOH/Na₂CO₃ solutions behaves similarly to silicon in waterglass, so these waste glasses can be used as activators in alkali-activated systems. Tchakoute et al. [3] proved that sodium silicates from waste glass and rice husk ash were suitable alternative alkaline solutions. The metakaolin-based geopolymer binders produced with alternative silicate solutions reached almost 40 MPa. Bouchikhi et al. [7] produced alternative silicate solutions by dissolving various amounts of residual waste glasses (RWG) in a 10 M NaOH solution. They proved the concept by producing metakaolin-based geopolymers reaching up to 35 MPa after 28 days.

In this work, we investigated the effect of RWG composition on the production process and the final properties of the alkali activating solutions produced from it.

2. Materials and Methods

Various alternative sodium silicate-based activators that can be used for producing inorganic polymers from slag were synthesized from residual waste glasses with the aim to increase the sustainability and lower the production cost of the current production route of NA165-5052. For this purpose, 2 types of RWGs, RWG1 and RWG2, were inserted in a bench top reactor (4520, Parr Instrument Company, Moline, IL, USA) together with NaOH solution (commercial, membrane grade) and were dissolved under various process conditions, such as NaOH concentration, glass fineness, process temperature and time. The resulting slurries were filtered and subjected to analyses, whereas the solutions that were closest to the NA165-5052 solution were used in the synthesis of inorganic polymers. The as-received RWG1 was contaminated with unidentified organic impurities and therefore was subjected to a pre-treatment consisting of burning with a gas burner for 20 min prior to any experiments. RWG2 was used in an as-received state.

The chemical composition of the RWGs as well as the filtrates (residues after reactions) was assessed by means of XRF (Bruker S8, Bruker, Billerica, MA, USA) and is listed in Table 1. The mineralogical composition was assessed using X-ray diffraction (XRD, Bruker D2 Phaser, Bruker, Billerica, MA, USA) in a 2θ range of $10\text{--}70^\circ$. The produced activating solutions were analyzed with respect to their solid content and $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio by means of potentiometric titration (Metrohm 808, Metrohm, Herisau, Switzerland).

Table 1. Chemical composition of the as-received RWGs and RWGs filtrates, in wt%.

	RWG1	RWG1 Filtrate	RWG2	RWG2 Filtrate
SiO ₂	62	51	58	46
CaO	15	27	8	8
Na ₂ O	12	5	13	23
Al ₂ O ₃	3	7	6	9
MgO	2	3	2	2
SO ₃	1	1	<1	<1
Fe ₂ O ₃	1	1	7	6
K ₂ O	1	<1	2	2
MnO	-	-	3	3
others	3	4	1	1

Inorganic polymer mortar samples were synthesized by activating an Fe-rich slag [8] with the alternative alkali solutions following the mortar preparation procedure listed in EN-196-1. Additionally, two more mortars were produced, where the Fe-rich slag was partially replaced with filtrated residue (from the synthesis process of alternative solutions) in order to identify whether the residue can be incorporated in the inorganic polymers. A reference mortar sample using the NA165-5052 activating solution was also made. The compressive and flexural strength of the mortars was determined after 7 and 28 days of reaction on an Instron 5985 testing device using a 250 kN load cell and a crosshead speed of 2 mm/min.

3. Results and Discussion

The chemical composition of the RWGs is listed in Table 1. Regarding the mineralogy, RWG2 was fully amorphous, while RWG1 contained small amounts of crystalline phases, such as quartz (SiO₂) and wollastonite.

The heat-treated RWG1 powder had d_{50} of 180 μm and density of 864 kg/m^3 , while the RWG2 powder had d_{50} of 65 μm and density of 376 kg/m^3 , which had an effect on both the optimal processing parameters as well as the properties of the resulting activating solu-

tion. Therefore, the processing parameters were optimized for each RWG separately. The parameters and the resulting activating solution characteristics are listed in Table 2 below.

Table 2. Process conditions and resulting characteristics of the produced alkali solutions—targeted properties were $\text{SiO}_2/\text{Na}_2\text{O} = 1.65$, solid content = 35 wt%.

	RWG1			RWG2		
	Achieved Molarity	Solid Content wt%	Dissolved RWG wt%	Achieved Molarity	Solid Content wt%	Dissolved RWG wt%
Time	16.5% NaOH (aq), 160 °C					
2 h	1.16	23	45			
3 h	1.25	29	50			
5 h	1.25	26	51			
NaOH (aq)	205 °C, 3.5 h			140 °C, 3 h		
10%	1.48	18		1.47	18	
~15%	1.21	24		1.21	26	
~20%	0.93	28		1.02	27	
Temperature	16.5% NaOH (aq), 3.5 h			16.5% NaOH (aq), 3 h		
140 °C	1.18	25	47	1.21	25.8	43
160 °C	1.27	26	51	1.20	24.7	-
180 °C	1.23	26	51	-	-	-
205 °C	1.19	22.5	45	-	-	-

The solution characteristics of the commercial NA165-5052 solutions, i.e., $\text{SiO}_2/\text{Na}_2\text{O} = 1.65$ and dry matter content of ~45 wt%, were achieved. It is clear from Table 2 that none of the tested conditions resulted in the targeted solution characteristics. Therefore, the most optimal process conditions per RWG were selected. These were: 160 °C and 3 h in 16% NaOH solution for RWG1 and 140 °C and 3 h in 16% NaOH solution for RWG2. Both produced solutions that were unstable and a precipitate was formed in both of them after a few hours. This could be related to the impurity of the used RWGs and/or to the relatively low molar ratio ($\text{SiO}_2/\text{Na}_2\text{O} \sim 1.25$) of the produced solutions. Therefore, a sufficient amount of silica fume was added to both alternative solutions to adjust their molarity (towards the targeted one) and to improve the solutions' stability.

Furthermore, despite the effort to find the optimal reaction conditions, the amount of dissolved RWG never exceeded 51 wt%. In order to better understand this phenomenon, the undissolved materials, i.e., filtrates, were characterized and the chemical composition is listed in Table 1. By comparing the composition of input RWGs and the filtrates it can be seen that the RWG1 filtrate is richer in CaO and Al_2O_3 and the RWG2 filtrate was richer in Na_2O and Al_2O_3 compared to the input materials, indicating preferred dissolution of some elements, e.g., SiO_2 . Mineralogical analyses of the filtrates revealed the formation of new phases (semi-crystalline and crystalline), see Figure 1. Several hydration phases, e.g., C-A-S-H, N-A-S-H, Tobermorite 11Å and zeolites, e.g., analcime, were identified in both filtrates, which suggests that part of the RWGs were alkali activated during the dissolution process for the synthesis of the alternative solution and formed a new, stable IP.

To prove the presented concept, the produced alkali solutions were used in IP-based mortar production. The compressive strengths of the mortars after 7 and 28 days of reaction are presented in Figure 2 below. Both alternative solutions performed comparably to the used reference solution. At 7 days, the mortar activated with the RWG1 solution reached the highest compressive strength, while the reference and the RWG2 mortar reached a similar strength of 17 MPa. However, after 28 days, the strength of the reference mortar was the highest, reaching almost 23 MPa, followed by the RWG2 and RWG1 mortars with 20 MPa. In order to utilize the undissolved materials (filtrates) an attempt was made to incorporate them in the production of IP mortars. One can see that 10 wt% addition of filtrate showed a negligible effect on the 7 days compressive strength; however, it showed

a negative effect at later strength, when this reached only 89% of the strength of the RWG1 sample. Higher additions of filtrates resulted in the lowering of both early as well as late strength, reaching 70% and 77% of the RWG1 sample strength, respectively.

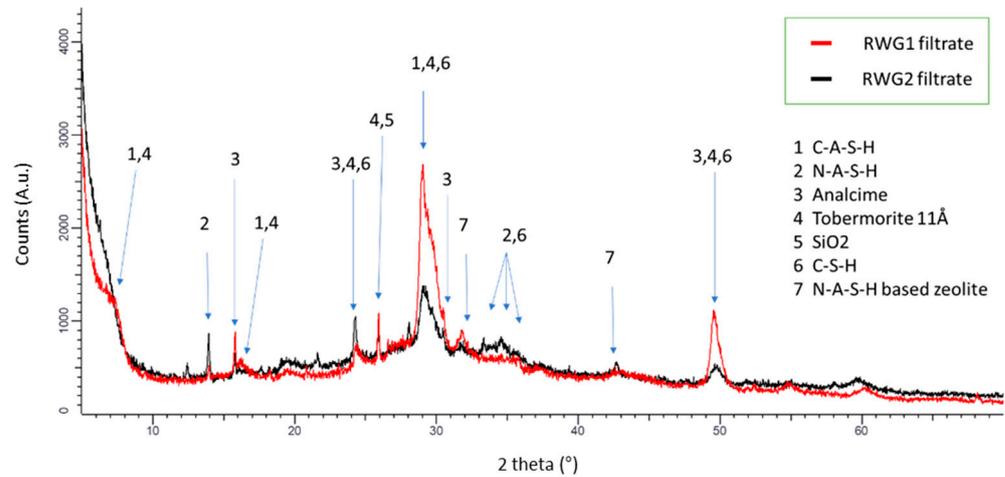


Figure 1. XRD pattern of the RWG1 and RWG2 filtrates.

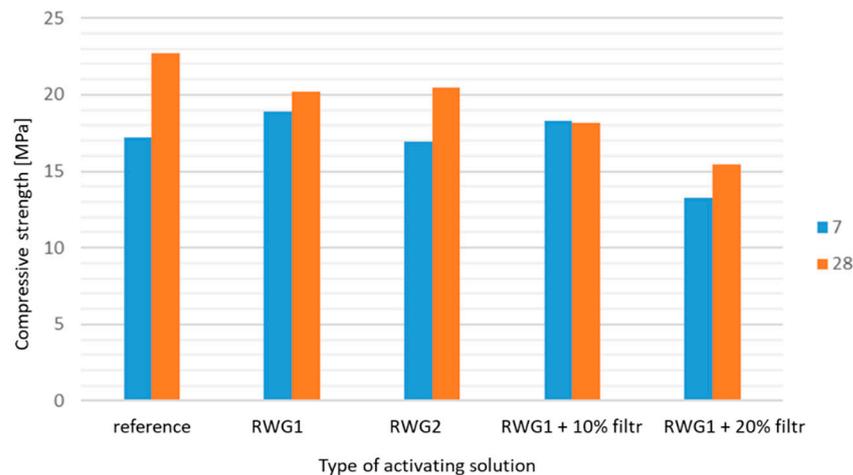


Figure 2. Compressive strength of IP synthesized with alternative activating solutions.

4. Conclusions

Two types of RWGs, differing in chemical, mineralogical composition, density and fineness, were studied for their potential to be used as raw materials in the production of alternative alkali solutions via a hydrothermal production process. The process parameters were optimized per RWG and the most optimal production conditions were identified to be 3 h at 160 °C and 3 h at 140 °C for RWG1 and RWG2, respectively. The low stability of the produced solution was solved by increasing the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio by means of silica fume addition. Despite all the effort, the max amount of dissolved RWG did not exceed 51 wt%. The analyses of the filtrates revealed the presence of hydration products, e.g., C-S-H, C(N)-A-S-H and zeolites in the filtrates, which explained the limited dissolution of the RWGs. Compressive strength of IP mortars produced from the RWG solutions reached similar values compared to the reference mortar. Addition of filtrate to the IP mortar up to 10 wt% did not influence early strength, but had a negative effect on late strength. Higher addition of filtrates to the IP mortar showed a negative effect on both early and late strength values.

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