Effect of Organic Retarders on Fluid-State and Strength Development of Rock-Based Geopolymer

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Abstract. Granite waste is rich in aluminum and silicate has the potential of turning to geopolymer material after mixing with an alkali solution. One of the challenges in developing a geopolymer is to select a suitable retarder to adjust the target pumpability while maintaining workability and followed by a proper strength development rate. In this study, the effect of five selected organic retarders on workability, viscosity, and compressive strength has been examined. Sucrose, a calcium chelator, gluconic acid, sodium lignosulphonate, and ionic liquid were selected as candidate retarders. The experiments were carried out at room temperature according to American Petroleum Institute (API) standards for testing well cement. The tested retarders indicated a secondary effect on fluid-state properties. The reasons for the secondary effect are due to either the change in the pH of slurries or the interaction between ions released from the retarder and the geopolymer precursor. Gluconic acid and sucrose provided a longer setting time, while they significantly lowered the strength development in the short-term. Lignosulfonate had less impact on workability. However, it reduced viscosity and yield stress. All retarders influenced the strength development rate, but the sodium lignosulfonate, chelator, and ionic liquid had a negligible impact on final strength after 14 days of curing.

Keywords: Rock-based Geopolymer, Retardation, Alternative Setting Material, Cement Replacement Material.

1   Introduction

Green transition, moving toward low carbon footprint technologies, has become a global trend for decades. Hence, research activities around alternative materials for conventional cement and concrete were conditioned by researchers around the world. Geopolymer is a class of cementitious materials that shows potential for integration in industries such as the building and construction sector as well as oil and gas well applications [1-3].

Geopolymer is synthesized using aluminosilicate-rich materials such as fly ash, metakaolin, etc., with alkali hydroxide or alkali silicate solutions as a hardener. Potassium and sodium are the common alkali elements used to design the hardener.

Geopolymers are under examination to adjust their properties depending on the application and the exposed environment. Long-term durability, sufficient strength, shrinkage issues, and adequate pumping time are just part of the topics that must be addressed in research studies. Retardation in geopolymerization reaction is a challenge for utilization. Based on the application of geopolymers, it is vital to study suitable retarders to achieve target setting time while maintaining the desired mechanical and rheological properties.

Different chemical admixtures have been introduced to enhance geopolymer systems' pumping time or workability. These additives are either organic such as hydroxycarboxylic acids [4], different sugars [5], sulphonate bio products [6], etc, or inorganics such as phosphate salts or the salt of heavy elements like zinc [7]. Every system is identical due to ingredients, application, and environmental condition; therefore, it is not accurate to draw a general conclusion about the effect of chemical admixture on all geopolymer systems. Unique parameters like the type of aluminosilicate minerals that exist in the precursor, type and concentration of silicates in hardener, the concentration of alkali hydroxide in the hardener, pH, free water content, and temperature define the effectiveness of the suggested chemical admixtures [8]. Additionally, the secondary effect of the chemical retarders on other rheological properties and mechanical properties after solidification remains unclear and depends on chemical and mineral composition.

A mix design of rock-based geopolymer has been studied previously using inorganic salts as a retarder [7]. In this study, the same geopolymer precursor discussed in reference [7] mixed with a hardener with the molar ratio (Silica, Si/Potassium, K) of 0.95 is selected to study the effect of five organic retarders on rheological properties and early mechanical strength. Sucrose, calcium chelator (TRP), gluconic acid (GLA), sodium lignosulfonate (NaLS), and 1-ethyl-3-methylimidazolium tetra chloroaluminate (IL) have been chosen after reviewing literature. Although some of the selected organic retarders have been studied for different geopolymer systems such as fly ash and metakaolin, the absence of data on the influence of selected chemicals on the rock-based geopolymer is considered a gap of knowledge in this study.

2   Materials and experiments

All samples were mixed based on an established procedure for the two-part geopolymer concept. The solid phase, also known as a precursor, contained waste powder from a granite mine, slag from the steel industry, and microsilica. The normalized chemical composition of the solid phase is presented in **Table 1**. The liquid phase, also termed hardener, was a mix of potassium silicate solution, potassium hydroxide, and water. The molar ratio of silica to potassium, Si/K, was adjusted equal to 0.95 and the total water content was 245 gr. The pH of the hardener was set at 13.95. The solid-to-liquid ratio was 2.34, and it was constant throughout the whole experiment.

D-sucrose, ethylenediaminetetraacetic acid – disodium salt dihydrate calcium chelator (98%), gluconic acid (50% solution), sodium lignosulfonate (industrial product supplied by an oil service company), and 1-ethyl-3-methylimidazolium tetra chloroaluminate were selected as candidate organic compounds for retardation.

Table 1. Chemical composition of the solid precursor

Chemical Components	Wt%
SiO2	62.995
Al2O3	12.965
CaO	1.493
MgO	3.957
K2O	10.424
Na2O	2.341
Fe2O3	3.811
TiO2	0.798
Other elements	0.425
LOI	0.79
Total	100

Rock-based geopolymer was mixed using blender specified in API RP10B-2 [9]. The mixing process is as follows; the liquid hardener was poured into the mixing jar and the precursor was added gradually for 15 seconds at 4000 RPM. The mixing was followed at 12000 RPM for 35 more seconds. This is the procedure generally used for mixing cement in a drilling cement laboratory [9].

Six different mixtures were prepared, and the viscosity, pumpability (workability), strength development rate, and compressive strength up to 7 days were tested at the equal curing condition of pressure, temperature, and humidity. The neat slurry (without any chemical admixture) has a density of 1.93 s.g. (~16 ppg). **Table 2** summarizes the physical properties of the mix and the concentration of the candidate retarders.

**Table 2**. Specification of the geopolymer mix - dosage of the retarders.

Solid-to-liquid ratio		2.34
Density (s.g)		1.93
pH hardener		13.95
Si/K (molar ratio)		0.95
Total water content (gr)		245
pH (neat recipe)		13.05
Retarder (% BWOS*)	Sucrose	2
	TRP	0.5
	GLA	1.5
	NaLS	1.5
	IL	0.25
* By weight of solid precursor		

2.1   Experimental Procedures

Viscosity test. After mixing, the slurries were transferred directly to viscosity measurement. The viscosity of slurries was tested using a rotational viscometer model Chan 35. It was a non-pressurized rotational viscometer consisting of a cylindrical bob concentrically placed within a sleeve, also called rotor. The slurry was poured into the viscometer's cup. The assembly of rotor and bob is immersed in the slurry in

such a way that the gap between the bob and rotor was filled with the geopolymer slurry. The rotor rotates at different rotational speeds. Rotation of the rotor shears the slurry within the gap, which applies torque to the bob. The bob is connected to a spring and the torsional stiffness of spring represents dial deflection. The dial deflection is converted to the shear stress in pascals unit through a conversion factor. In this study, the R1-B1 configuration of the bob and rotor was used. Such configuration means that the inner diameter of rotor and the outer diameter of bob are 36.83 mm and 34.49 mm, respectively. The viscosity test was performed in the range of 3 to 300 RPM. For the selected configuration, this range is equal to the range of 5.11 s^{-1} to 511 s^{-1}. **Fig. 1** illustrates the picture and schematic of the rotational viscometer used in this study.
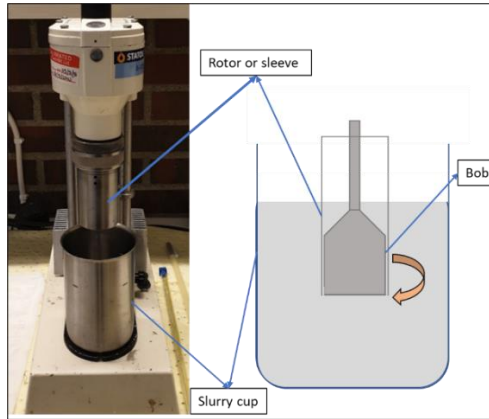

Fig. 1. Rotational viscometer model Chan 35 for measuring the viscosity of slurries at different shear rates.

Thickening time. To measure the thickening time (workability), the consistency of slurries was measured continuously using atmospheric consistometer specified in API RP 10B-2 [9]. The machine consists of a slurry cup, a cup lid equipped with a spring to measure the torque, a paddle for shearing the slurry, and a water bath to keep the temperature constant. The slurry is sheared at constant rotational speed and the torque is measured continuously. **Fig. 2** shows the schematic of the consistometer.

Uniaxial compressive strength (UCS). The compressive strength of samples was tested using MTS servo-hydraulic testing machine. Three cylindrical samples were tested at a constant loading rate of 7 N/s [10]. The diameter of the samples was 50.1 mm and the length of the samples was set at 100 mm. The compressive strength was reported as the ratio of measured force perpendicular to cross-sectional area, Eq. (1).

$$\sigma = \frac{F}{A} \tag{1}$$

were σ is the axial stress in mega pascal (MPa), F is the measured axial force in kilo Newton (KN), and A is the cross-sectional area in square millimeters (mm^2).
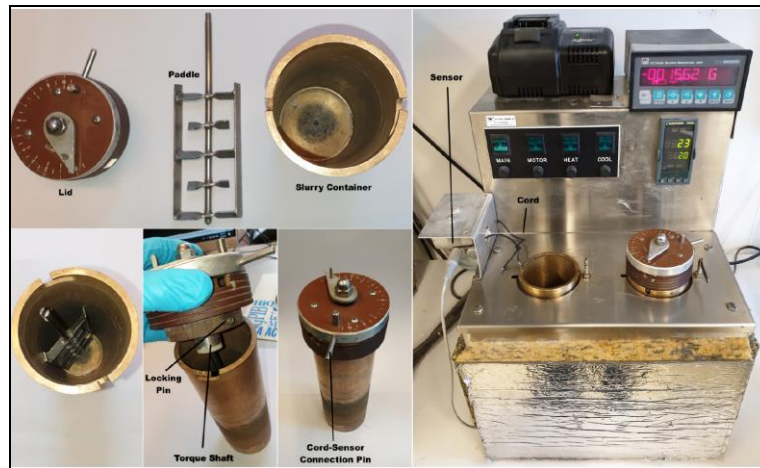
Fig. 2. Atmospheric consistometer used for measuring the workability of geopolymer slurry.

Sonic strength development (UCA). The apparatus used for the UCA test was a twin-cell ultrasound cement analyzer. This technique provided information about the rate of strength development by continuously measuring the velocity of the sonic wave through the sample. The stronger the material, the higher the speed of the sonic wave, and the shorter the transit time. After mixing, the slurry was poured into the equipment's cell and connected to the transducers for measuring sonic wave velocity. A predefined algorithm then converted the transit time to the compressive strength through a polynomial equation introduced to the software. However, this equation is created based on the chemistry of conventional cement, and the compressive strength values are not representative of the real strength of materials with different chemistry and solidification reaction. Hence, the data in this test is only valid for indicating the hardening and the rate of solidification. **Fig. 3** shows the schematic of the UCA including the main equipment and the cell.
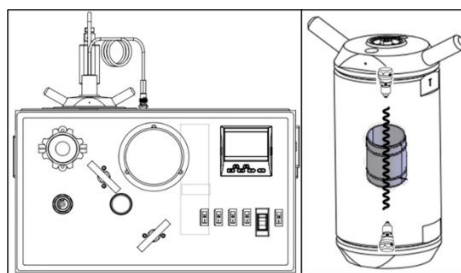
Fig. 3. Schematic of the ultrasonic cement analyzer (UCA). The figure on the right shows the cell of the equipment.

3 Results and Discussion

3.1 Viscosity test

It is well accepted that chemical additives used as a retarder can have a secondary effect on other properties, such as rheological behavior and viscosity of the mix. The viscosity of geopolymers is highly dependent on their chemical composition, including the chemistry and particle size of the solid phase, the composition of hardener, and the nature of chemical additives.

The Herschel – Bulkley approach was used to model the viscosity of slurry by the curve fitting method [11]. This method is widely used to model the viscosity profile of non-Newtonian slurries over a range of shear rates by a three-parameter equation, Eq. (2).

$$\tau = \tau_y + k\dot{\gamma}^n \qquad (2)$$

In this equation, τ_y is the yield stress, k is the consistency factor, and n is the curvature component. These parameters are used to model the rheological behavior of the slurry during pumping and placement. Gel strength development of the slurries was also measured after 10 seconds and 10 minutes. The values are summarized in **Table 3**.

Table 3. Herschel - Bulkley parameters and gel strength values for the tested slurries.

Slurries	Herschel – Bulkley Parameters			Gel Strength Development (Pa)	
	τ_y (Pa)	n	k	10 S	10 Min
Neat geopolymer	4.653	0.866	0.350	5.11	7.12
Sucrose	4.146	0.848	0.389	5.11	6.643
TRP	5.029	0.844	0.417	5.11	6.643
GLA	4.010	0.866	0.306	4.088	6.132
NaLS	2.161	0.936	0.234	2.55	6.643
IL	6.990	0.818	0.471	7.665	9.198

IL and TRP systems showed the highest yield stress, while the system with NaLS has the lowest yield stress compared to the neat geopolymer system. The yield stress values for sucrose, GLA, and neat systems were almost the same. For cementitious materials, depending on the particle size of the solid phase and dissolution rate of the ingredients, low values of yield stress may jeopardize the risk of particle sedimentation and result in an inhomogeneous structure after solidification. The shear stress – shear rate and the viscosity profiles are shown in **Fig. 4** and **Fig. 5**, respectively.
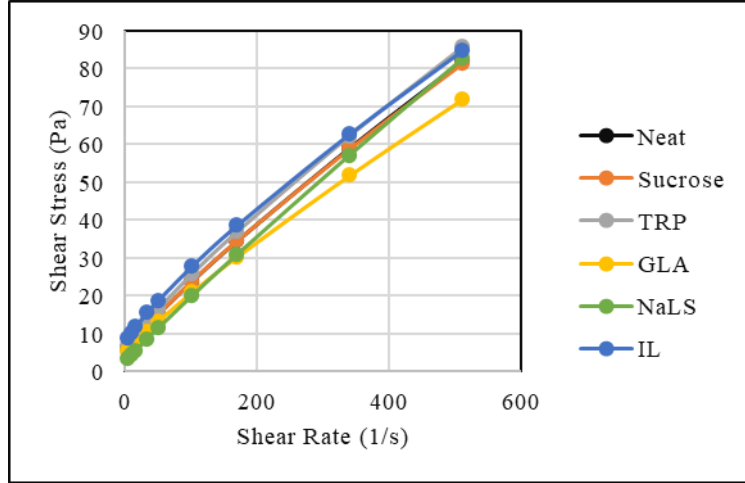
Fig. 4. Shear stress – shear rate profile of slurries with different retarders.
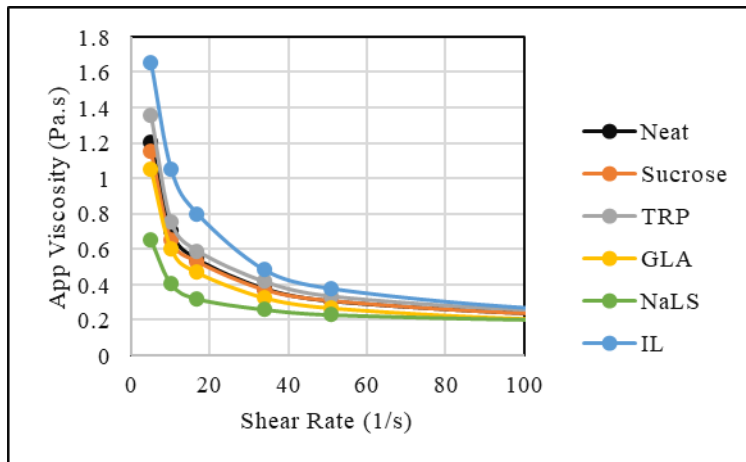

Fig. 5. Viscosity profile of the slurries with different retarders at low shear rates.

All systems show shear thinning behavior to various extents. The sucrose has minimum impact on the viscosity profile of the tested geopolymer. At the lower shear rates, solidum lignosulfonate and gluconic acid reduced the viscosity and shear stress at constant shear rates, compared to the neat system. However, sodium lignosulfonate shows almost the same shear stress at higher shear rates as the neat system. Sodium lignosulfonate and gluconic acid have been used as a plasticizer in construction industry [12]. In these systems, sodium lignosulfonate benefits from the electrostatic repulsive forces between particles in the mix, which results in decrease in a shear stress, while in GLA mix, steric repulsive force is the mechanism .

The systems including chelator (TRP) and ionic liquid (IL) showed higher viscosity and shear stress at constant shear rates compared to the neat system. TRP chelator captures positive charge ions such as K^+, Mg^{2+}, and Ca^{2+} ions in the mix introduced by adding slag and the hardener and forming large complex molecules. Such com-

plexes can result in higher shear stress in the slurry. When the ionic liquid dissolves in the solution, positive charge imidazole and the anion aluminum tetra chloride are dispersed in the mix. The imidazole ion is adsorbed on the silicate surface with a negative charge [13]. Depending on the length of the alkyl chain connected to the imidazole ion, the viscosity of the fluid can be affected at different shear rates. In previous studies, the researchers showed that increasing the length of the alkyl chain results in lower yield stress and lower viscosity of the mix . The observed behavior in our system is consistent with previous experimental research, where in our study the alkyl chain is ethyl. Therefore, we expect that in the case of using longer chains such as butyl, octyl, and dodecyl in the structure of IL, the system would show lower viscosity compared to the current IL system.

3.2   Pumpability

Workability or pumpability of geopolymer slurry is a critical parameter indicating how long the slurry is pumpable after mixing under specific environmental pressure or temperature. The consistency profile of the rock-based geopolymer using candidate retarders is presented in **Fig. 6**.
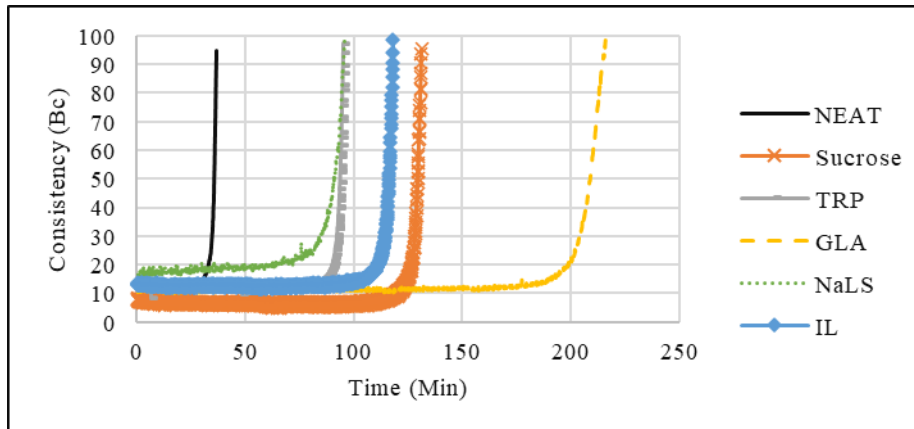

Fig. 6. Consistency profile of the rock-bashed geopolymer with selected retarder additives.

The consistency values of all samples are started between 10 and 20 in Bearden unit of consistency (Bc), which could be an indication of an acceptable viscosity profile for pumping. The consistency profile highlights the behavior of geopolymer after mixing up to gelation. The consistency remains almost constant for some time when the aluminosilicate precursor is dissolved in the alkaline environment of the mix and monomers are started to form. At the same time, the dissolved aluminate and silicate connect and form smaller building units of geopolymer to generate oligomers. Increasing the concentration of oligomers in the presence of alkali cations, the slurry becomes thick, and solidification starts through poly-condensation and hydration reactions. At this point, the consistency starts to increase. Generally, the consistency value of 100 Bc is considered as setting time, when the slurry becomes unpumpable. The neat mix design was only pumpable for about 30 minutes and followed by quick

gelation and hardening in only 5 minutes by reaching 100 Bc. In the petroleum industry and in well construction, such behavior is called a right-angel-set of cementitious material. The desired retarder should postpone the hardening while keeping the rate. Using a retarder, the hardening rate can be affected in a way that the consistency profile starts to deviate from the right-angel set.

Both NaLS and TRP chelator additives increased the pumping time by 200 %, from 30 min to about 90 min. In both systems, the complexation of Ca^{2+} and Mg^{2+} with lignosulfonate and ethylene diamine tetra acetic acid (EDTA) was suggested as the mechanism for retardation [14]. IL extended the pumping time by about 280 % and the slurry was pumpable for almost 115 minutes. The positive charge imidazole ions cover aluminosilicate source particles and reduce the dissolution rate and at the same time, hinder nucleation and structure growth due to their large size. In the case of using sucrose as a retarder, the pumping time was slightly more than IL, and the pumpability reached 130 minutes. In the case of gluconic acid (GLA), the pumpability reached its maximum, which is 210 minutes after mixing the slurry. It is equal to 600 % increase in pumpability of this mix design.

A common fact about all candidate retarders is reducing the pH when they were dissolved in the water. Such reduction in the pH results in a lower dissolution rate of aluminosilicate particles, and hence, less aluminate and silicates participate in geopolymerization reaction. Therefore, the pH reduction is suggested as a mechanism for retardation of geopolymerization.

3.3   Ultrasonic Strength Analysis (UCA)

In the previous section, right-angel set was observed in all mix designs. However, there is a transition time between a so-called hard gel at 100 Bc in the consistency test and the point that the material starts to develop strength detectable by the ultrasound. Chemicals used as a retarder to extend the pumping time may have a secondary impact on the strength development rate and the final strength of the geopolymers [15]. **Fig. 7** illustrates the sonic strength development of the geopolymer with three retarders. The data for sucrose and gluconic acid were excluded from the UCA test results since no strength development was observed after seven days of testing.

The neat geopolymer slurry started to develop strength after about 20 hours, although the mix was only pumpable for 30 minutes. This highlights a huge transition between forming strong gel and setting and starting strength development. The ingredient used to blend the precursor of the rock-based geopolymer is one of the reasons for delayed strength development at low temperatures [16]. Reactivity and the phase at which the silicates exist are critical parameters. This issue can be solved by adjusting the water content and reactivity of the ingredients in solid phase, for example, by calcination. TRP delayed strength development by 7 hours compared to the neat mix design while the strength development rate was the same. NaLS and IL started to develop strength after 33 hours. Both systems delayed strength development by 13 hours compared to the neat recipe, however, for the IL system, the rate of strength development reached the neat and TRP systems. For the NaLS mix, the early strength development rate was lower than all other systems, but the rate was increased later

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and the sonic strength of NaLS system became the highest at the end of the testing period.
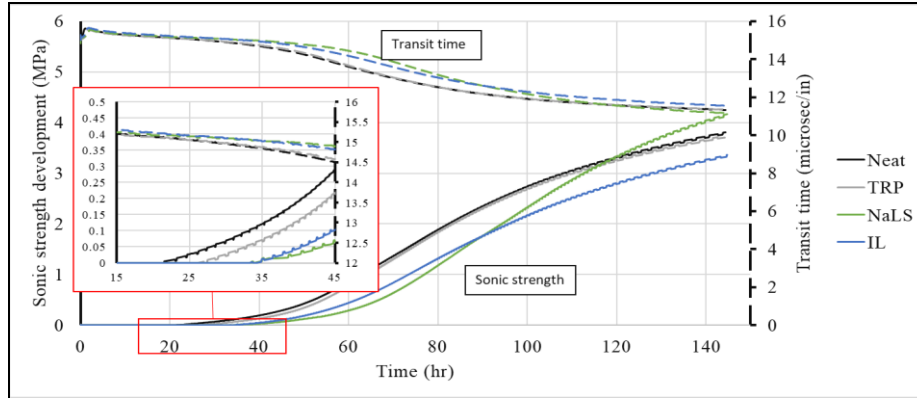
Fig. 7. Sonic strength development of rock-based geopolymer mixed with different candidate retarders.

It is worth mentioning that the slurry in the consistometer cup is continuously sheared by the paddle, which increases the possibility of interaction between ingredients. Such mixing is not present in the ultrasonic cement analyzer, and the slurry becomes in static mode after pouring into the equipment's cell.

3.4   Uniaxial Compressive Strength (UCS)

The uniaxial compressive strength of the mix designs was tested after 7 and 14 days of curing at ambient temperature and pressure and in sealed containers. The results of the UCS test are presented in **Fig. 8**. The figure excludes the results of the GLA mix since the samples were not able to hold any loading. The 7-day UCS and UCA tests were performed to estimate the strength of the material for the same period. By comparing the achieved results from both UCS and UCA tests, it is evident that the absolute sonic strengths estimated by the UCA equipment were unreliable for reporting. Therefore, it is necessary to generate a unique algorithm for materials with different chemistry compared to conventional cement [15].

The average compressive strength for the neat, TRP, and NaLS systems was about 11.5 MPa after 7 days. The UCS values remained almost constant up to 14 days. Using the selected dosage of these retarders had no significant impact on the short-term compressive strength of the geopolymer. The effect of IL on the 7-day strength was not significant and the average compressive strength was about 10 MPa. The compressive strength did not change significantly and reached 11.5 after 14 days of curing. However, using sucrose and GLA had a severe negative effect on early strength development. Gluconic acid in alkaline environment and the presence of Ca^{2+} ions forms complexes. High stability of these complexes negatively affects early strength development, especially in the absence of elevated temperature. Depending on the mix design, gluconic acid may not be a suitable retarder at low temperatures.
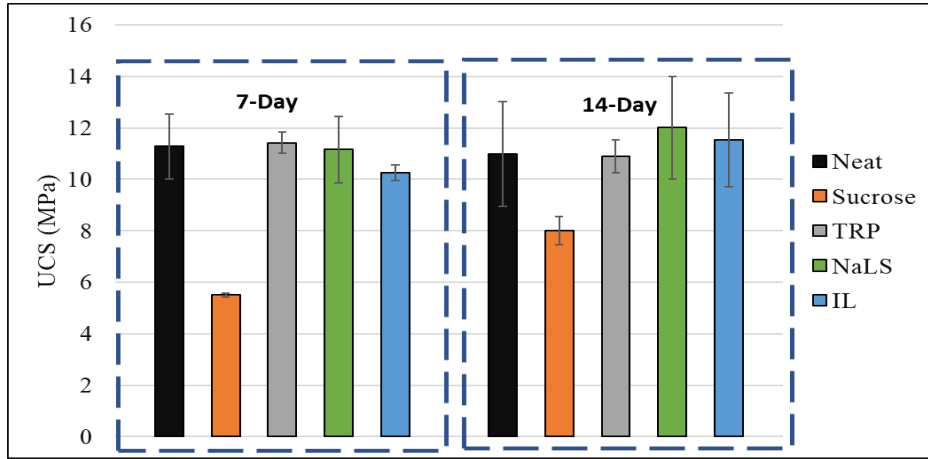
Fig. 8. 7-Day and 14-Day UCS test of geopolymer mix designs with candidate retarders.

The compressive strength of sucrose-based mix after 7 days of curing reached 5.5 MPa, which was about a 50 % of the strength of the neat recipe. In alkaline environment, molecules of sucrose convert to a stable acid complex and adsorb on the surface of particles rich in aluminosilicate [5]. In this way, the dissolution rate of these particles is reduced significantly and results in slow strength development. Moreover, sucrose is able to form insoluble metalorganic compounds in an alkaline environment. These metalorganics cover the particles and hinder geopolymerization reaction. After 14 days, the UCS of sucrose-based samples reached 8 MPa, which was equal to 45% increase compared to the 7-day samples.

4   Conclusions

Five selected organic chemicals were selected as retarders for a rock-based geopolymer and the effect of specific dosage on workability, viscosity, and UCS was tested. Selected retarders increased workability compared to the neat geopolymer recipe. Though the slurry with GLA gave the highest setting time of 210 minutes, it was not able to withstand the desired compressive strength up to 14 days. All retarders affected viscosity profile of the geopolymer to a various extent. Sucrose extended the workability, but it had huge negative effect on the UCS. There was no relation between gelation and strength development rate. Although TRP, NaLS, and IL chemicals delayed the strength development, the early compressive strength of geopolymer was not changed significantly and remained in the range as the neat recipe. Except for the samples mixed with sucrose, the compressive strength remained constant.

References

1.   Davidovits, J., *Geopolymer cement.* A review. Geopolymer Institute, Technical papers, 2013. **21**: p. 1-11.

2. Khalifeh, M., Saasen, A., Vrålstad, T., Larsen, H.B., and Hodne, H., *Experimental study on the synthesis and characterization of aplite rock-based geopolymers.* Journal of Sustainable Cement-Based Materials, 2016. **5**(4): p. 233-246.

3. Salehi, S., Khattak, J., Saleh, F.K., and Igbojekwe, S., *Investigation of mix design and properties of geopolymers for application as wellbore cement.* Journal of Petroleum Science and Engineering, 2019. **178**: p. 133-139.

4. Schneider, N. and Stephan, D., *The effect of d-gluconic acid as a retarder of ground granulated blast-furnace slag pastes.* Construction and Building Materials, 2016. **123**: p. 99-105.

5. Kusbiantoro, A., Ibrahim, M.S., Muthusamy, K., and Alias, A., *Development of sucrose and citric acid as the natural based admixture for fly ash based geopolymer.* Procedia Environmental Sciences, 2013. **17**: p. 596-602.

6. Zulkarnain, N.N., Shafiq, N., Abd Rahman, S.H., and Farhan, S.A., *Lignosulfonate as a retarder in geopolymer cement for oil well cementing: Effect on compressive strength.* Materials Today: Proceedings, 2022.

7. Chamssine, F., Khalifeh, M., and Saasen, A. *Rheological and Mechanical Properties of Rock-Based Geopolymers Developed for Well Abandonment: Effect of Chemical Admixtures at Elevated Temperatures.* in *ASME 2022 41st International Conference on Ocean, Offshore and Arctic Engineering.* 2022.

8. Salehi, S., Khattak, M.J., Rizvi, H., Karbalaei, S., and Kiran, R., *Sensitivity analysis of fly ash geopolymer cement slurries: Implications for oil and gas wells cementing applications.* Journal of Natural Gas Science and Engineering, 2017. **37**: p. 116-125.

9. American Petroleum Institute, A., *API RP 10B-2, Recommended Practice for Testing Well Cements*, in *Washington, DC: API.* 2013, API.

10. American Petroleum Institute, A., *API TR 10TR7, Mechanical Behavior of Cement*, in *Washington, DC: API.* 2017, API.

11. Herschel, W. and Bulkley, R. *Measurement of consistency as applied to rubber-benzene solutions.* in *Am. Soc. Test Proc.* 1926.

12. Nelson, E.B. and Guillot, D., *Well Cementing.* 2006: Schlumberger.

13. He, D., Liang, R., Zhao, J., Liu, Z., Lu, Z., and Sun, G., *Effect of ionic liquids in compatibility with PCE and cement paste containing clay.* Construction and Building Materials, 2020. **264**: p. 120265.

14. Luukkonen, T., Abdollahnejad, Z., Ohenoja, K., Kinnunen, P., and Illikainen, M., *Suitability of commercial superplasticizers for one-part alkali-activated blast-furnace slag mortar.* Journal of Sustainable Cement-Based Materials, 2019. **8**(4): p. 244-257.

15. Kamali, M., Khalifeh, M., Saasen, A., and Delabroy, L., *Materials for Well Integrity-Characterization of Short-Term Mechanical Properties*, in *Proceedings of the ASME 2020 39th International Conference on Ocean, Offshore and Arctic Engineering OMAE2020.* 2020.

16. Kamali, M., Khalifeh, M., Saasen, A., and Silva Santos Moreira, P.H. *Long-Term Mechanical Properties of Barrier Materials for Cementing Operations–Analysis of Morphology and Micro-Structure.* in *International Conference on Offshore Mechanics and Arctic Engineering.* 2022. American Society of Mechanical Engineers.