PROCEEDINGS, 49th Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 12-14, 2024
SGP-TR-227

Geopolymers as Alternatives to Cements

Allison S. Brandvold and Waltraud M. Kriven

University of Illinois at Urbana-Champaign, Dept. of Materials Science and Engineering, Urbana, IL 61821, USA

Email: asb11@illinois.edu, kriven@illinois.edu

Keywords: Geopolymers, inorganic polymers, aluminosilicates, thixotropy, thermal stability

ABSTRACT

Geopolymers are 3-dimensionally bonded, aluminosilicate, inorganic polymers and cured at ambient temperatures. They are made from calcined clay and an aqueous, alkaline, metasilicate solution precursor. A typical composition is centered around $M_2O\bullet Al_2O_3\bullet 4SiO_2\bullet 13H_2O$ where M is an alkali metal such as Na, K or Cs. The strained nature of the 5-coordination aluminum cation polyhedra is identified as the reason why metakaolin-based geopolymer ceramics are made from highly alkaline solution, rather than with high temperature diffusion as is typical for ceramics. Geopolymers are made under high shear mixing, are scalable into large batch sizes and can be 3D printed. While cements are 2D-bonded inorganic polymers of silicates and aluminates forming calcium silicate hydrates and calcium aluminates, geopolymers are 3D, covalently-bonded, aluminosilicate polymers which set at room temperature. Geopolymers essentially behave as an acid-resistant, refractory glue which can be reinforced with a variety of sand, gravel, chopped basalt fibers or platelets. Geopolymer composites exhibit significant graceful failure and fracture toughness such as three times that of alumina. Geopolymer composites can adhere to metals and form an acid-resistant coating as well as undergo self-healing. Geopolymers can be heated up to ~1,000°C after which they crystallize into an aluminosilicate ceramic, such as nepheline or leucite. Geopolymers can be made into porous water purification filters for removing heavy metals such as arsenic, cadmium, mercury etc. Current work is in progress to make geopolymers by valorization of mine tailings. Geopolymers may be a rapidly setting, acid resistant, thermally stable, alternative to cements and concrete for applications in geothermal wells.

1. INTRODUCTION

Geopolymers are a new class of inorganic polymers intermediate between ceramics and cements. They are inorganic polymers that cross link under ambient temperatures into a ceramic-like material which is refractory and acid resistant. They are scalable and made under ambient temperatures like a cement, but behave like a ceramic (Figure 1). They are alkali-activated aluminosilicates made from metakaolin clay or mine tailings and alkali silicate solutions, and have a nominal formula of $M_2O\bullet Al_2O_3\bullet 4SiO_2\bullet 11H_2O$ where M = Na, K, Cs. Geopolymer composites are stable to 1000°C above which they crystallize into ceramic composites. They can be reinforced with ceramic, metal, polymeric or biological particulates, chopped fibers, weaves or meshes as well as the usual sand and gravel used in concretes. They can be pre-fabricated in polymeric molds or 3D/4D printed. To produce 1 ton of geopolymer liberates only 0.25 tons of CO_2 as opposed to the 1 ton of CO_2 liberated for 1 ton of cement. Geopolymers exhibit significantly increased acid resistance showing only 2% degradation over one year as opposed to ~50% for cements under the same strongly acidic conditions. Alkali activated cementitious materials are made from waste materials of slag and class F fly ash, and consistent almost entirely of cement binder having the usual formular C-S-H or $CaO\text{-}SiO_2\text{-}H_2O$. Geopolymer concretes retain ~ 6MPa of flexural strengths to 1150°C.

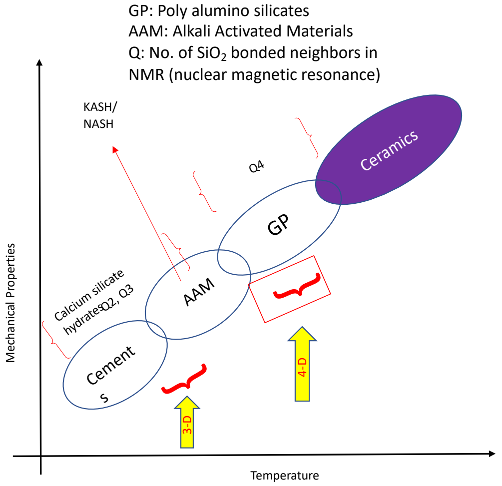

Figure 1. Schematic description of relationship between cements, alkali activated cements, geopolymers and ceramics. Geopolymers are scalable and made under ambient temperatures like a cement, but can have mechanical properties, like a ceramic.

1.1 Rheology

Geopolymers have been largely identified as a shear-thinning and thixotropic fluid that has a yield stress[1–5], although a small controversy exists in the field about potential Newtonian properties[6] of geopolymers. Current literature pertaining to geopolymers or cement-like materials is very limited and can be split into two sections: metakaolin-based geopolymers (GP)[1–3,5–9] and or alkali activated materials (AAM) or alkali-activated cements (AAC).[4,10–13] AAMs use slag and fly ash as the aluminosilicate source instead of metakaolin and are known to possess different chemical structures, setting time and mechanical properties than geopolymers.[14–16] Figure 2 shows the breakdown of inorganic polymer terminology for clarification. Due to the inconsistent sources and hence purity and varying properties associated with slag and fly ash, GPs were of primary focus of this work, but literature with slag and fly ash-based systems was also considered for a holistic understanding of the work already conducted and the types of experiments used to understand the rheological properties of AAMs.

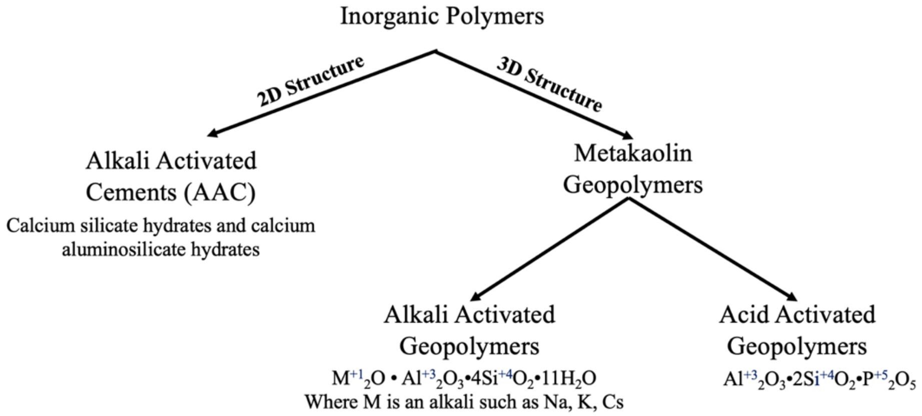

Figure 2. The terminology of inorganic polymers based on structural differences[17,18]

A significant consideration for rheological testing is rheometer geometry selection. Franchin et al.[1] employed a parallel plate-based system but reported poor adhesion with the rheometer head and unreliable data. Ranjbar et al., working on AAMs, also reported difficulties with the parallel plate geometry because of premature sample hardening due to drying[10]. To combat the difficulties of measuring the properties with the parallel plate geometry, the vane rotor geometry was found to be a much more reliable choice for cementitious materials due to its ability to reduce wall slip, make bulk measurements and minimize shearing upon sample loading.[19–21] For literature that used the vane rotor or some other type of building cell geometry (helical impeller or such), there is much evidence of structuration of GP or AAMs due to thixotropy as a result of increases in yield stress as a function of time, but compositions of pastes widely varied and experimental set up was not uniform for comparison.[2,12,13,22]

For temperature-related analysis of rheological properties, two studies have conducted a small range of oscillatory experiments[7] and shearing experiments[9], both of which were conducted on GPs with either a helical impeller or coaxial cylindrical geometry. The oscillatory measurements indicated that elevated temperatures raise both the storage and loss moduli (elastic and dissipated energy[23], respectively, that change as a result of the internal structure of the fluid) of geopolymers over time[7], but tested a very narrow temperature range of 25 - 40°C which limits what could be considered reasonable terrestrial printing temperatures. A wider temperature range (higher and lower) would help understand what other global temperatures are viable for printing. The constant shear experiments conducted by Romagnoli et al. found that an increase in temperature led to an increase in viscosity[9] likely due to increasing the rate of the geopolymerization reaction. Romagnoli et al., however only conducted testing on the temperature range of 20 – 35°C and did not fully explore the influence of shearing time in combination with temperature. It is advantageous to have a full understanding of rheological properties as a function of temperature and shear time for large scale 3D printing, which is likely to be conducted in a non-temperature-controlled environment which may impact viable printing time.

Within the subset of GPs, studies have shown sodium (Na)-based GPs to have higher viscosity and yield stress values overall than potassium (K)-based geopolymers (KGP) when using non-commercially synthesized waterglass[2]. The higher viscosity of Na-based systems makes rheological testing very limited to avoid surpassing rheometer torque limits and attain reliable results. In addition, it has been shown that KGPs are more stable at higher temperatures than their Na counterparts.

1.2 High Temperature High Pressure

Depending on the stoichiometry, geopolymers that undergo significant heating will transform into different crystallized structures, such as leucite for potassium, pollucite for cesium and nepheline for sodium geopolymers at ambient pressures.[24–27] At high pressure, however, many other crystalline minerals are able to be synthesized such as jadeite for sodium geopolymer[28,29] and leucite, hollandite, orthoclause and coesite for potassium geopolymer.[30] Very few investigations have looked into the various crystallization transformations that occur with geopolymers undergoing high temperature and high pressure, indicating a significant gap in the field.

2. DISCUSSION

2.1 Thixotropy

Much effort has already been put towards characterizing the influence of variables such as time, shear rate, stress and temperature dependent behavior of KGP paste. For all of the rheological testing conducted, a composition of $K_2O\bullet Al_2O_3\bullet 4SiO_2\bullet 11H_2O$ was selected since it will transform into leucite[31] at high temperatures (discussed later). KGP pastes underwent a systematic study to determine the extent of reversible thixotropy versus irreversible chemical setting, with considerations of shear rate, stress and time. Rheological tests conducted include shear ramp cycling, shear ramps with time delay, cyclic oscillations, constant shear rate and viscosity recovery with a variable shear rate experiment.[32] These results were compared with Ultrasonic Wave Reflectometry (UWR)[33–35], which determined that full chemical setting occurred at approximately 25 hours and confirmed that early rheological changes in GPs were not primarily due to chemical bonding.

It was found that geopolymers have significant thixotropic properties likely resulting from hydrogen bonding intermolecular forces between alumina and silica tetrahedra that are released during mixing. Upon high shear mixing the metakaolin dissolved, releasing $Al(OH)_4^-$ and $Si(OH)_4$ tetrahedra, in which the OH groups from either the Al or Si were attracted to one another and the tetrahedra were slowly oriented to favor the hydrogen bonding attraction. This allowed the $Al(OH)_4^-$ and $Si(OH)_4$ units to build a physically attracted internal network, until one of the OH^- group reacted with an H^+ from a neighboring tetrahedron, breaking off to form water and synthesizing a poly(sialate) monomer unit (or a polysialate derivative) through a chemical reaction.[32] The extent of the structural build up was heavily dependent on time as shown in Figure 3. by the increase in stress curve with an increase in time.

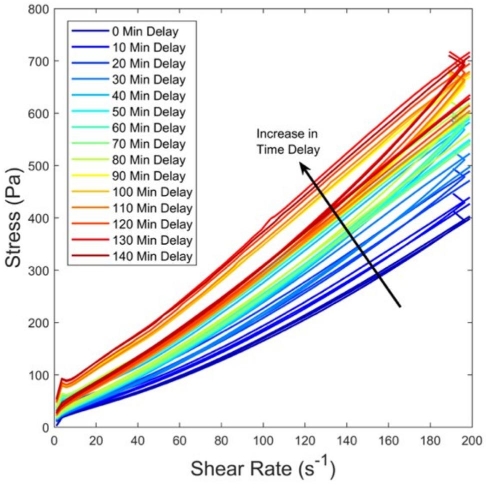

Figure 3. Shear rate vs stress for all segments in the shear ramp vs time delay experiments[32]

It was also found that full thixotropic restructuring occurs at around 90–100 min of total undisturbed rest time (Figure 4). and reaching a state of full thixotropic disturbance heavily depending on subjected processing parameters[32].

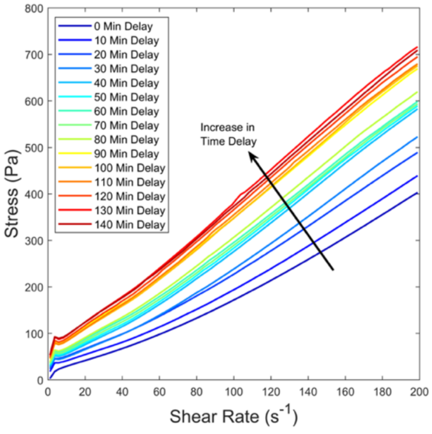

Figure 4. Shear rate vs stress for the first ramp up segment in the shear ramp versus time delay experiments[32]

Lastly, cyclic storage and loss modulus investigations also proved the reversibility of the changing viscosity based on consistent and repeated cross over points between the storage and loss modulus during oscillatory testing, which is favorable for tailoring viscosity.

2.2 Temperature dependence

For the temperature dependent investigation, KGP pastes were subjected to constant shear, constant oscillation, and stress ramp testing (for yield stress) in the temperature range 5-55°C. This temperature range was selected to mimic potential viable printing temperatures. Results concluded that an increase in temperature would lower the overall starting viscosity of KGP paste but would shorten the time before there was an exponential increase in viscosity, which was due to the geopolymerization reaction starting to dominate the fluid properties (Figure 5). The time at which the paste hits an exponential increase in viscosity was also dependent upon shear rate. Lower shear rates caused less disruption to the geopolymerization reaction, allowing the chemical reaction to ensue much faster versus higher shear rates at the same elevated temperatures. At lower temperatures, it was apparent that the starting viscosity was higher due to the increased amount of energy required to overcome the hydrogen bonding attraction between less mobile tetrahedra units as a result of the reduced amount of thermal energy put into the GP system.

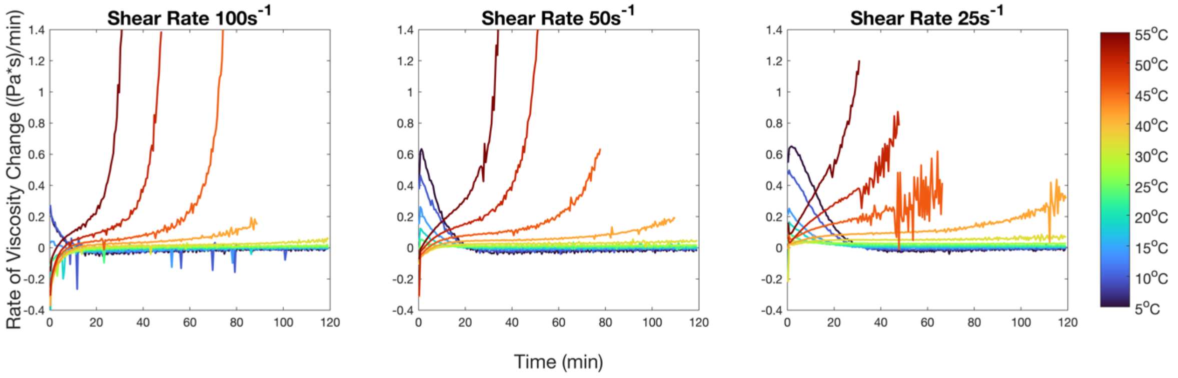

Figure 5. Viscosity versus time curve for KGP pastes at three different shear rates[36]

Evidence for higher temperatures causing molecular-level structuring in a short time came from oscillatory experiments (Figure 6). These showed that higher temperatures induced a rapid increase in storage and loss moduli after about 20 minutes, indicating significant structural build up as a result of hydrogen bonding and the geopolymerization reaction. At the highest temperature tested, 55°C, the storage and loss moduli had an increase of four orders of magnitude within 55 minutes, which was significant compared to the single order of magnitude increase that occurred after 120 minutes for samples held at 20°C.

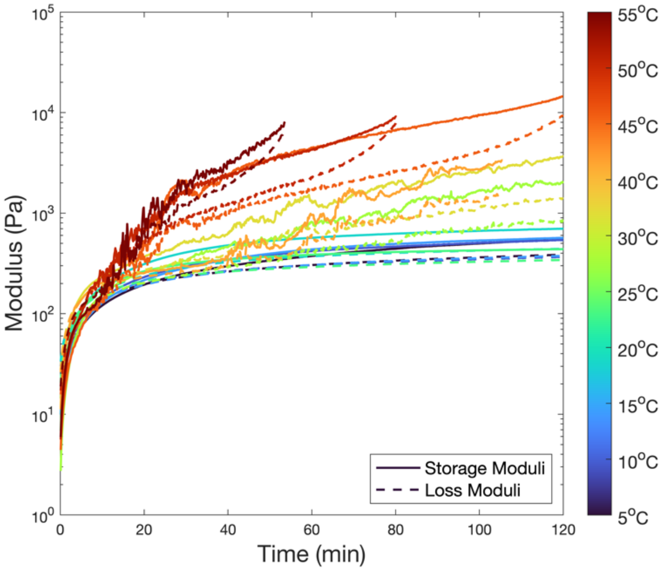

Figure 6. Modulus versus time curve for constant oscillation at various temperatures (oscillation at 0.01% strain and angular frequency of 6.28 rad/s).[36]

2.3 Set time evaluation

In order to evaluate the full set time of geopolymers Vicat needle testing was used. Vicat needle testing presents a few limitations for use with geopolymers given that geopolymers are less viscous than cement and the Vicat apparatus is designed/calibrated specifically for cement paste.[37,38] It is still useful for a basic understanding of the changes in penetration resistance that occurs in geopolymers. The Vicat needle curves are shown in Figure 7 and the calculated Vicat set times based on the equation in ASTM C191[39] are summarized in Table 1.

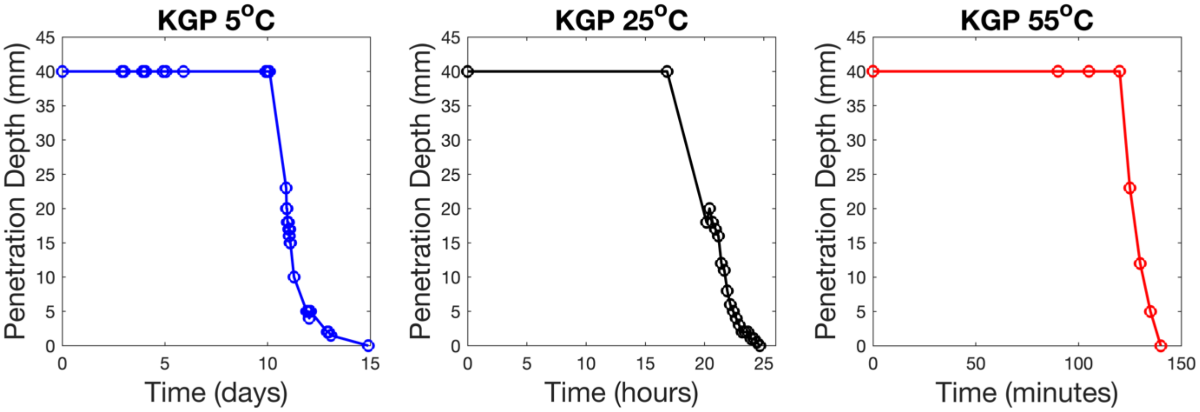

Figure 7. Penetration resistance curves for KGP held at either 5, 25 or 55 °C[36]

Table 1. Calculated Vicat needle set time.

Temperature (°C)	Calculated Vicat Set time
5	11 days, 2 hours, and 4 minutes
25	19 hours and 6 minutes
55	2 hours and 4 minutes

The results indicated a strong relationship between temperature and set time as predicted. The 55 °C sample went from full penetration through the sample at 120 minutes to no penetration at 140 minutes, leaving a small window for any penetration measurement. At first consideration, this behavior in the Vicat needle data seemed to indicate a rapid geopolymerization reaction towards the end of the experiment, however this was likely not to be the case, as early consistency changes in the geopolymer paste did not change the viscosity enough to resist full penetration of the needle and 300 g mass given its cement based calibration. This window of measurable penetration resistance is hypothesized to be a measurement of the final polymerization steps such as consolidation and hardening as a result of immobility of the now chemically bonded poly(sialate) units.[5,40] It is critical to use both the sensitivity of the rheometer to evaluate early changes in rheological properties of KGPs and the Vicat needle to measure the consolidation and hardening steps[5,40] that surpass torque limits on the rheometer for a full understanding of the cure time. The calculated Vicat set time[39] for this sample was 2 hours and 4 minutes, which was largely aided by the influx of thermal energy.

The 5 °C sample, however, had a much more elongated window, showing full penetration starting at around day 10 and no penetration at nearly 15 days, giving almost a 5-day window for measuring some kind of resistance to the Vicat needle, which was significantly larger than for the 55 °C sample. The lack of thermal energy impeded the mobility of tetrahedra units, minimizing the progress of the geopolymerization reaction and greatly delaying solidification. The calculated set time was found to be 11 days, 2 hours and 4 minutes. Lastly, the 25°C sample fell in between the 5 and 55 °C, with a calculated set time of 19 hours and 6 minutes. Overall, the Vicat needle indicated that the full hardening of KGP pastes was heavily dependent on the environmental temperature.

The temperature-based testing of KGP proved a significant dependence between environmental temperature and rheological properties. Hot temperatures (35-55 °C) can significantly reduce the viscosity for the first several minutes, but quickly give way to rapid geopolymerization and exponential increase in resistance to flow. These rapid changes (such as viscosity increase and yield stress increase), drastically reduce the viable printing time for materials held at these high temperatures, ranging from 30-60 minutes depending on exact temperature. The incremental rheological changes associated with the moderate temperatures (20-30 °C), indicate a viable printing window of about 12-15 hours after synthesis of KGP. Lastly, the significantly elongated geopolymerization reaction associated with cold temperatures (5-15 °C) implied a printing window that could be as long as 7-10 days or so before some hardening of the KGP paste will occur.

3. CONCLUSION

3.1 Rheology

Geopolymers have been proven to be a shear thinning, thixotropic material which many rheological properties that can be tailored by various processing parameters. The primary mechanism driving the thixotropic recovery of geopolymers is the hydrogen boding attraction of silica and alumina tetrahedra versus the chemical setting of the geopolymerization reaction. In addition, the rheological properties are significantly altered with various shear rates and shearing environment. The setting time can also be slowed down or expedited with a change in temperature.

REFERENCES

1. Franchin G, Scanferla P, Zeffiro L, Elsayed H, Baliello A, Giacomello G, et al. Direct ink writing of geopolymeric inks. J Eur Ceram Soc. 2017 Jun;37(6):2481–9.

2. M. D. M. Paiva LDFR LI Castrillon Fernandez, RD Toledo Filho, ECCM Silva, R Neumann, and OA Mendoza Reales. Rheological properties of metakaolin-based geopolymers for three-dimensional printing of structures. ACI Mater J. 2021 Nov 1;118(6).

3. Tran K, Chalamet Y, Mignard N, Carrot C, Gyppaz F, Auvray T. Kinetics of geopolymerization followed by rheology: a general model. Soft Matter. 2022;18(13):2549–57.

4. Zhang DW, Zhao KF, Xie F zhu, Li H, Wang D min. Rheology and agglomerate structure of fresh geopolymer pastes with different Ms ratio of waterglass. Constr Build Mater. 2020 Jul;250:118881.

5. Rouyer J, Poulesquen A. Evidence of a fractal Percolating network during geopolymerization. Struble L, editor. J Am Ceram Soc. 2015 May;98(5):1580–7.

6. Favier A, Habert G, d'Espinose de Lacaillerie JB, Roussel N. Mechanical properties and compositional heterogeneities of fresh geopolymer pastes. Cem Concr Res. 2013 Jun;48:9–16.

7. Poulesquen A, Frizon F, Lambertin D, Lambertin D. Rheological behavior of alkali-activated metakaolin during geopolymerization. J Non-Cryst Solids. 2011;

8. Steins P, Poulesquen A, Diat O, Frizon F. Structural evolution during geopolymerization from an early age to consolidated material. Langmuir. 2012 Jun 5;28(22):8502–10.

9. Romagnoli M, Leonelli C, Kamse E, Lassinantti Gualtieri M. Rheology of geopolymer by DOE approach. Constr Build Mater. 2012 Nov;36:251–8.

10. Ranjbar N, Mehrali M, Kuenzel C, Gundlach C, Pedersen DB, Dolatshahi-Pirouz A, et al. Rheological characterization of 3D printable geopolymers. Cem Concr Res. 2021 Sep;147:106498.

11. Palomo A, Banfill PFG, Fernández-Jiménez A, Swift DS. Properties of alkali-activated fly ashes determined from rheological measurements. Adv Cem Res. 2005 Oct;17(4):143–51.

12. Kashani A, Provis JL, Qiao GG, van Deventer JSJ. The interrelationship between surface chemistry and rheology in alkali activated slag paste. Constr Build Mater. 2014 Aug;65:583–91.

13. Muthukrishnan S, Ramakrishnan S, Sanjayan J. Effect of alkali reactions on the rheology of one-part 3D printable geopolymer concrete. Cem Concr Compos. 2021 Feb;116:103899.

14. Mackenzie KJD, Welter M. Geopolymer (aluminosilicate) composites: synthesis, properties and applications. In: Advances in Ceramic Matrix Composites [Internet]. Elsevier; 2014 [cited 2021 Oct 7]. p. 445–70. Available from: https://linkinghub.elsevier.com/retrieve/pii/B9780857091208500186

15. Sankar K, Sutrisno A, Sutrisno A, Kriven WM. Slag-fly ash and slag-metakaolin binders: Part II—Properties of precursors and NMR study of poorly ordered phases. J Am Ceram Soc. 2019;

16. Nodehi M, Taghvaee VM. Alkali-Activated Materials and Geopolymer: a Review of Common Precursors and Activators Addressing Circular Economy. Circ Econ Sustain. 2022 Mar;2(1):165–96.

17. Waltraud M. Kriven (2018) 5.9 Geopolymer-Based Composites. In: Beaumont, P.W.R. and Zweben, C.H. (eds.), Comprehensive Composite Materials II. vol. 5, pp. 269–280. Oxford: Academic Press.

18. Davidovits J. Geopolymer Chemistry and Applications, 5th Ed. St.Quentin, France: Geopolymer Institute; 2020.

19. Owens CE, Hart AJ, McKinley GH. Improved rheometry of yield stress fluids using bespoke fractal 3D printed vanes. J Rheol. 2020 May;64(3):643–62.

20. Barnes HA, Carnali JO. The vane-in-cup as a novel rheometer geometry for shear thinning and thixotropic materials. J Rheol. 1990 Aug;34(6):841–66.

21. Barnes HA, Nguyen QD. Rotating vane rheometry — a review. J Non-Newton Fluid Mech. 2001;

22. Lu C, Zhang Z, Shi C, Li N, Jiao D, Yuan Q. Rheology of alkali-activated materials: A review. Cem Concr Compos. 2021 Aug;121:104061.

23. Chen T. Rheology: Basic Theory and Applications Training [Internet]. 2020 Rheology Online Training 1; Online (TA Instruments). Available from: https://www.tainstruments.com/wp-content/uploads/2020-Rheology-Online-Training-1.pdf

24. Kriven WM. Geopolymers and geopolymer-derived composites. In: Encyclopedia of Materials: Technical Ceramics and Glasses [Internet]. Elsevier; 2021 [cited 2022 Aug 11]. p. 424–38. Available from: https://linkinghub.elsevier.com/retrieve/pii/B9780128185421001004

25. Kriven WM, Bell JL, Mallicoat SW, Gordon M. Intrinsic microstructure and properties of metakaolin-based geopolymers. Int Workshop Geopolymer Bind Interdepend Compos Struct Prop. 2007;71–86.

26. Bell JL, Driemeyer PE, Kriven WM. Formation of Ceramics from Metakaolin-Based Geopolymers. Part II: K-Based Geopolymer. J Am Ceram Soc. 2009 Mar;92(3):607–15.

27. Xie N, Bell JonathanL, Kriven WM. Fabrication of Structural Leucite Glass-Ceramics from Potassium-Based Geopolymer Precursors: Structural Leucite Glass-Ceramics Converted from K-Geopolymer. J Am Ceram Soc. 2010 Apr 12;93(9):2644–9.

28. Zhao T, Yan X, Cui S, Niu W. The physical and chemical properties of synthetic and natural jadeite for jewellery. J Mater Sci. 1994 Mar;29(6):1514–20.

29. Zhao L, Ma H, Fang C, Ding L, Jia X. Synthesis and characterization of purple NaAlSi2O6 jadeite under high pressure and high temperature. J Cryst Growth. 2018 Oct;499:30–4.

30. Liu L gun. High-pressure phase transitions of kalsilite and related potassium bearing aluminosilicates. Geochem J. 1978;12(4):275–7.

31. Musil SS, Kriven WM. *In Situ* Mechanical Properties of Chamotte Particulate Reinforced, Potassium Geopolymer. Biernacki J, editor. J Am Ceram Soc. 2014 Mar;97(3):907–15.

32. Brandvold AS, Al-Chaar GK, Kriven WM. Isolating the effects of thixotropy in geopolymer pastes. J Am Ceram Soc. 2023 Jan 23;106(5):2797–807.

33. Popovics JS, Subramaniam KVL. Review of Ultrasonic Wave Reflection Applied to Early-Age Concrete and Cementitious Materials. J Nondestruct Eval. 2015;

34. Subramaniam KVL, Lee J. Ultrasonic assessment of early-age changes in the material properties of cementitious materials. Mater Struct. 2007;

35. Sankar K, Stynoski P, Kriven WM. Sodium silicate activated slag-fly ash binders: Part III—Composition of soft gel and calorimetry. J Am Ceram Soc. 2019 Jun;102(6):3175–90.

36. Brandvold AS, Kriven WM. Influence of temperature on rheological properties during early-stage geopolymerization.

37. Sleiman H, Perrot A, Amziane S. A new look at the measurement of cementitious paste setting by Vicat test. Cem Concr Res. 2010 May;40(5):681–6.

38. Kang X, Lei H, Xia Z. A comparative study of modified fall cone method and semi-adiabatic calorimetry for measurement of setting time of cement based materials. Constr Build Mater. 2020 Jul;248:118634.

39. C01 Committee. Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle [Internet]. ASTM International; [cited 2023 May 16]. Available from: http://www.astm.org/cgi-bin/resolver.cgi?C191-21

40. Duxson P, Fernández-Jiménez A, Provis JL, Lukey GC, Palomo A, van Deventer JSJ. Geopolymer technology: the current state of the art. J Mater Sci. 2007 May 1;42(9):2917–33.