

Development of One-Part Rock-Based Geopolymers for Downhole Cementing Applications

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The use of geopolymers as a full replacement for cement in oil well cementing applications requires the development of not only environmentally friendly but also user-friendly cementitious materials. This study aims to investigate the early-age mechanical and chemical properties of synthesized one-part geopolymers, which are heat-cured rock-based products. These geopolymers were synthesized from granite-based precursors and were activated by solid powders of potassium silicate, with a small portion of potassium hydroxide (KOH) as an accelerator to enhance the setting time and early strength. The mechanical and chemical properties of the one-part geopolymers were characterized, and the mineralogy of the solidified samples was analyzed through crystallography to better understand their microstructure. The study found that the investigated one-part geopolymer mixes, which were activated by a solid activator with a modulus ratio of 2.4, developed acceptable compressive strength of around 7 to 13 MPa within 24 h and up to 7 days. The use of one-part geopolymers has the potential to provide environmentally- and user-friendly slurries that can facilitate their utilization for large-scale in-situ applications in the petroleum and civil engineering sectors. [DOI: 10.1115/1.4062250]

Keywords: geopolymer review, well integrity, water content, chemical admixture, just add water, petroleum engineering, petroleum wells-drilling/production/construction

1 Introduction

The demand for Ordinary Portland Cement (OPC) and the consumption of limestone reserves are increasing very rapidly. These demands besides the high increases in carbon taxes have been tightly challenging the concrete industry on daily basis [1]. Several mandatory carbon emissions reduction policies have been introduced by governments and regulators. These regulations are to support the cementing industry toward more focusing on stimulating investment and innovation by researching and adopting these carbon emissions reduction policies [2,3]. OPC production and processing operations are dependent on the decarbonation of limestone and fuel used during the calcination and production of cement which releases high carbon dioxide emissions. OPC has been considered one of the main contributors to global carbon dioxide emissions with up to 8% [4,5]. It is very viable to develop low-carbon and low-energy types of cement alternatives to reduce the greenhouse effect [4,5]. Geopolymers are a type of cementitious material with the potential to fully replace OPC while having the potential to significantly reduce carbon dioxide emissions. In a study by McLellan et al. [6], the costs and greenhouse gas emissions of geopolymers were compared to OPC. The study found that geopolymer emits between 14 and 97 wt% less carbon dioxide than OPC. However, there is some uncertainty surrounding this finding due to the difficulty distinguishing between geopolymers and alkali-activated-based types of cement [7].

According to Duxson et al. [8], geopolymers are considered third-generation cement after OPC and lime. The term “geopolymer” generally refers to partially amorphous and partially crystalline solid aluminosilicate materials in tetrahedral form, also known as inorganic polymers. Some researchers do not distinguish between geopolymers and alkali-activated cement. Geopolymers

are low calcium content systems consisting of silicate monomers as repeating units (O–Si–O–Al–O). Several solid aluminosilicate materials such as feldspar, metakaolin, industrial residues, and solid wastes have been utilized as solid geopolymer precursors. However, these precursors have different reactivity depending on their chemical composition, mineralogy, morphology, and fineness [8,9]. The main criteria for producing and developing stable geopolymer is the solid precursor should be highly amorphous or reactive, have consistent chemical composition, and have low water content demand with a water-to-solid precursor ratio of less than 0.4 [10,11].

Geopolymer could be designed to obtain desired mechanical properties compared to OPC, including higher acidic attack resistance, heat resistance, higher mechanical strength, and lower chemical shrinkage [12,13]. Furthermore, it is important to prepare and select each component's proper type and dose, such as alkali-silicate activator, precursors, and admixtures [14]. Moreover, geopolymer technology could be useful for allowing waste beneficiation routes, known as circular economy, for using various industrial wastes and unused by-products [15,16]. However, supply chain availability for geopolymer precursor materials, suitable admixtures for these materials, and examining protocols are still inadequate to be generalized and standardized globally [17].

Binders were mainly formed from the chemical reaction between the alkali activation source and the aluminosilicate precursor, which were patented in 1908 by Kuhl [18]. Afterward, several pioneering developments were done by Glukhovskiy [19], Krivenko [20], Davidovits [21], and Palomo et al. [22], respectively. Table 1 presents some historical reviews and recent overview articles on geopolymer and alkali-activated materials.

Various types of raw materials have been utilized for synthesizing geopolymers, which may contain other types of synthetic powder precursors [29]. In the context of geopolymer synthesis, the most commonly used materials as powder precursors are metallurgical slags and fly ash. Metallurgical slags such as blast furnace slags (Ground Granulated Blast Furnace Slag, GGBFS) are mixtures of poorly crystalline materials with depolymerized calcium silicate glasses to control the strength development profile as is

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Table 1 Examples of published literature reviews and articles on alkali-activated materials and geopolymers

Title	Significant outputs
Mechanism of geopolymerization and factors influencing its development: a review [23]	A review of the development of geopolymers, including chemical reactions, source materials roles and effects, and mix compositions and combinations.
Alkali-activated binders: A review; (Part 1) historical background terminology reaction mechanisms and hydration products [24]; (Part 2) About materials and binders manufacture [25]	A general review of alkali-activated binders, including historical background, terminology, hydration products, materials and binders manufacture, and properties and durability
Mechanism and chemical reaction of fly ash geopolymer cement: A review [26]	An overview of utilization of fly ash geopolymer cement as alkali-activated binders
Geopolymer concrete: A review of some recent developments [10]	A review of utilization and development of geopolymer concrete as a potential construction material in several applications
Materials for optimized P&A performance: Potential utilization of geopolymers [27]	Development and utilization of rock-based geopolymers for zonal isolation and well abandonment were presented. Viscosity, pumpability, fluid loss, strength development, and durability of the geopolymers were studied
One-part alkali-activated materials: A review [28]	A review of the currently published state-of-art in the development of one-part geopolymer admixtures, including the employed solid precursors, activators, admixtures, mixing designs, and resulting binding materials

done in OPC [30]. Fly ash (FA) is a mixture of clay, sand, and organic matter that is presented in coal, produced as a by-product during the combustion process. These compounds are melted in a furnace and then quenched rapidly in air to obtain small spherical particles [31].

In geopolymer synthesis, there are two main classes for FA that can be used, which are dependent on their calcium content; Class F contains low calcium according to ASTM C618, and Class C contains high calcium content. However, Class C FA is rarely utilized in geopolymer synthesis as Class C could be classified compositionally comparable to some mixtures of Class F and GGBFS [32,33]. Moreover, fly ash class F and GGBFS mixtures are more preferred in the synthesis of geopolymers, where Class C fly ash is less abundant than fly ash Class F [7,10].

The nomenclature and terminology regarding geopolymers and alkali-activated materials are still subject to ongoing debates in the literature. The former is characterized by a three-dimensional tetrahedral silica structure with high content Q4(2Al) and Q4(3Al) centers and low calcium content. In contrast, the latter is characterized by lower silicon coordination, which is Q2 and Q2(1Al) centers, and higher calcium content [34].

Conventional geopolymers, also referred to as two-part geopolymers, are typically produced by partially dissolving solid precursors containing reactive aluminosilicates (known as part one) in a concentrated alkali solution. The alkali solution can include alkali silicate, carbonate, sulfate, or a combination of these compounds, which act as part two of the reaction [35,36]. However, the use of highly alkaline or alkaline silicate solutions poses logistical and environmental challenges. Thus, the development of one-part geopolymers that only require the addition of water has become crucial in recent years [9].

Purdon [37] prepared a mortar mixture by dry mixing sodium hydroxide powder, and slag and then adding water. A patent in the 1980s presented a dry mixture of metakaolin, amorphous silica, furnace slag, potassium silicate, and hydroxide, in addition to adding either fly ash, or calcined clay before and then adding water [38]. Another patent showed a mixture of amorphous silica from fly ash with sulfuric or hydrochloric acid [39].

In the 1970s, Davidovits conducted research on the formulation of one-part geopolymers by reacting metakaolin, alkali metal disilicate, and slag. He proposed the capability that sodium or potassium silicate powder could be used as solid activators due to their wide availability and unique activation properties [40].

Duxson and Provis [9] have presented other general specifications and approaches for one-part geopolymer mixtures. For instance, precursors can be prepared by melting feldspar with high calcium content before the combustion process. Reducing the amount of water in the mixture is also desired to conserve concrete properties and improve environmental sustainability. A lower water-to-binder ratio results in lower porosity and permeability of

the concrete. As a result, a one-part geopolymer design should have a low water-to-binder ratio and fine spherical particles [7].

Currently, two-part geopolymers have been implemented in various large-scale applications in Australia and Ukraine as evidenced by studies [28,41]. However, the challenges regarding the transportation and handling of corrosive alkaline solutions needed for mixing conventional geopolymers are a major drawback. These challenges highlight the importance of not only environmentally friendly cementing materials but also to be user-friendly ones. Thus, the development of user-friendly geopolymers is a crucial strategy to facilitate the utilization of geopolymers as a full replacement of cement for oil well cementing applications.

One-part “just add water” geopolymers are user-environmentally friendly cementing materials. They are more promising for in-situ applications due to overcoming the impracticalities of conventional two-part geopolymers [17,35,42]. However, they still need extensive investigations and developments to be more applicable for industrial use.

In this article, the aim is to provide a prior state-of-the-art in the development of one-part rock-based geopolymer mixtures. This study discusses the early-age effect of water content and four different chemical admixtures on the geopolymerization mechanisms, hydrated products, and their mechanical properties.

2 Materials and Methods

This study involves the solid phase, which consists of precursors, a solid activator, and admixtures, and the liquid phase, which contains deionized water and an accelerator. The precursors are obtained from granite rock and by-product materials. For the solid activator, anhydrous potassium silicate in powder form with a molar ratio (MR) of 3.92 was utilized. Four admixtures are used in this study: sodium hydroxide in pellet form, calcium carbonate in powder form, calcium oxide in powder form, and zinc oxide powder. Additionally, a small amount of 12M potassium hydroxide (KOH) solution is used as an accelerator. The chemical composition of the neat recipe (granite is a source of aluminosilicate, GGBFS is a calcium- and magnesium-rich material and amorphous aluminosilicate, and microsilica is a pure amorphous silicate material) is shown in Table 2, indicating the weight percentage of the three precursors in the mixture. The mineralogy of the precursors has been studied in detail [27,43–45].

2.1 Experimental Equipment. *API Mixer*—A high-shear API cement blender was used for mixing all the components to form the slurry in each experiment following API 10B-2 [27].

Curing of samples—All samples were heat cured in an oven at 70 °C Bottom hole circulating temperature (BHST). The samples

Table 2 Chemical composition of the precursor in wt%

Chemical composition (wt%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	LOI ^a
Precursor mix	56.63	12.47	1.09	6.23	16.45	1.77	2.87	1.16	0.29	0.6

^aLoss on ignition.

were cured inside cylindrical plastic molds and covered with plastic lids.

Uniaxial compressive strength (UCS)—A cutter machine was used to flatten both sides of the samples to be prepared for running UCS. The dimensions of these samples were 51 mm in diameter and about 80–85 mm in height. UCS tests were performed following API Spec 10A [46]. The samples were placed under compression using a mechanical tester with a loading rate of 10 kN/min.

Sonic Strength—To measure the sonic strength of the materials, an ultrasonic cement analyzer (UCA) specified in API 10B-2 [27] was employed to measure sonic strength development by use of sonic impedance at 14 MPa and 70 °C for 7 days. The equipment is designed and calibrated to test OPC [47]. Therefore, for any new material, new algorithms should be generated and applied in the custom algorithm option. The same equipment was used for all the materials to minimize any errors in the system.

Compositional Analysis—The accuracy of X-ray diffraction (XRD) data is dependent on various parameters including XRD instrumental intensity, time-steps, incremental angle, testing conditions, etc. In this study, XRD samples were dried in an oven at 30 °C overnight. Afterward, these specimens were kept in a vacuum dryer for one day to maximize the removal of water particles and to prepare them for XRD testing.

The crystalline phases of the sample were analyzed by a Bruker-AXS Micro-diffractometer D8 Advance, which uses CuK α radiation (40.0 kV, 25.0 mA) with a 2 θ range from 5 deg to 92 deg with 1 deg/min step and 0.010 deg increment. The main crystalline XRD patterns have been highlighted and investigated. EVA v5

software was used to analyze the crystalline components and to estimate the degree of crystallinity.

2.2 Experimental Procedures. The candidate recipes were mixed in the laboratory according to the recommended procedures [27,43,46,48]. The mixing procedures for all recipes were as follows: the precursors were mixed including chemically normalized components. The activator was a potassium silicate anhydrous powder with a molar ratio (MR = SiO₂/K₂O) of 3.9. A small portion of potassium hydroxide 12M solution (as an accelerator) was used to lowering down the molar ratio to 2.4.

2.2.1 Mixing. Mix design entails preparing the solid and liquid phases of the neat recipe, with and without adding admixtures to the solid phase, and at the end, combining all of them by blending. First, having obtained enough components, solids and liquids are mixed separately in a clean bucket and plastic container, respectively. Regarding admixtures, for each experiment, each admixture in powder form between 0.14 and 1.14wt% equivalent to the solid precursor was added to the solid phase in the initial mix design. Table 3 presents the type and total amount of additives added to the rock-based geopolymers with their recipes' names.

3 Results and Discussion

3.1 Uniaxial Compressive Strength Test. All recipes in Table 3 were investigated for Uniaxial compressive Strength (UCS); each recipe includes three samples for each mix design, which were prepared and cured at 70 °C, at atmospheric pressure. All samples were tested after 1 day of curing. Furthermore, the top 1-day UCS recipes were also investigated after 7 days of curing. Figures 1–5 present the average compressive strength of the materials given in Table 3 after a 1-day curing period. Moreover, the top comparable recipes (with 0.14wt% chemical admixture) from 1-day UCS results in addition to W1P (W1P-35%) were selected for further investigation for 7-day UCS data as shown in Figs. 6 and 7, respectively. One should note that 1-day strength development is critical for drilling purposes. Therefore, it was considered in this work.

UCS results show the effect of water content on the given mix design as shown in Fig. 1. It has been suggested that water only provides a medium for the dissolution and restructuring of aluminosilicate sources into geopolymers [49]. The given one-part rock-based

Table 3 Mix design for the given rock-based 1P GP

Mix design name ^{a,b}	Additives (wt%)	Additives in millimoles
W1P ^c	Non	Zero
W1Pb	Non	Zero
W1Pb-CO2	0.14 wt% CaO	35.71
W1Pb-CO4	0.57 wt% CaO	71.43
W1Pb-CO6	0.86 wt% CaO	107.14
W1Pb-CO8	1.14 wt% CaO	142.86
W1Pb-C2	0.14 wt% CaCO ₃	19.98
W1Pb-C4	0.57 wt% CaCO ₃	39.96
W1Pb-C6	0.86 wt% CaCO ₃	59.94
W1Pb-C8	1.14 wt% CaCO ₃	79.92
W1Pb-Z2	0.14 wt% ZnO	24.57
W1Pb-Z4	0.57 wt% ZnO	49.14
W1Pb-Z6	0.86 wt% ZnO	73.71
W1Pb-Z8	1.14 wt% ZnO	98.28
W1Pb-N2 ^d	0.14 wt% NaOH	50.03
W1Pb-N4 ^d	0.57 wt% NaOH	100.07
W1Pc ^e	Non	Zero

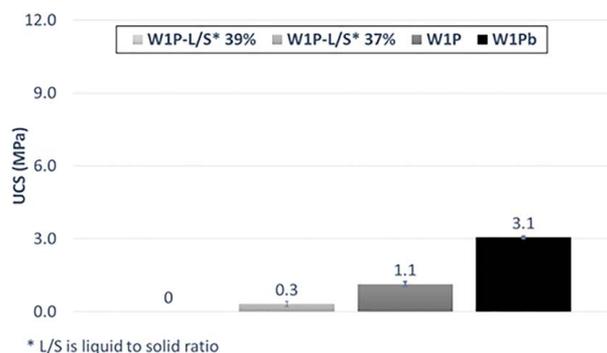
^aAll recipes had the same Activator and Accelerator to Solid precursors ratio, 0.20.

^bAll recipes had the same free water content, 88.19 wt% in the liquid phase.

^cW1P has 35wt% liquid-to-solid ratio. However, all W1Pb recipes have 33wt% liquid-to-solid ratio.

^dThe addition of NaOH pellets was considered as a partial substitution to the KOH solution to conserve MR = 2.4.

^eW1Pc has the same mix design as W1Pb with a solid accelerator either KOH or NaOH pellets instead of the liquid accelerator. The addition of these hydroxide pellets was considered as a complete substitution to the KOH solution with conserving MR at 2.4.

**Fig. 1 The effect of water content on 1-day UCS**

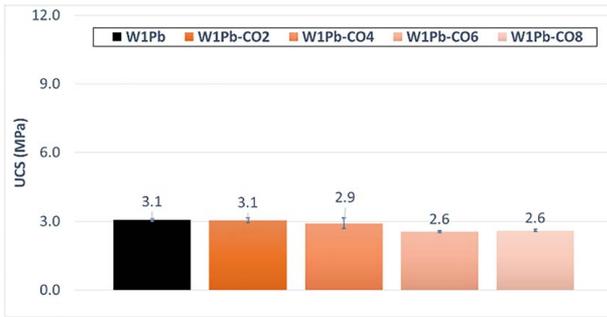


Fig. 2 The effect of chemical admixture CO on 1-day UCS

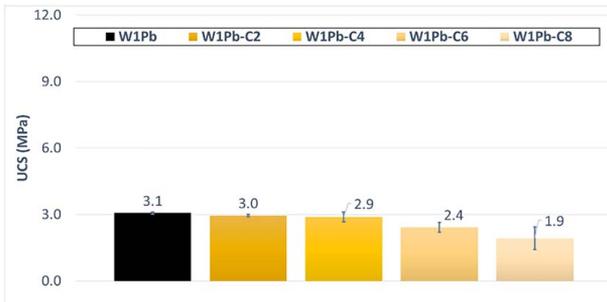


Fig. 3 The effect of chemical admixture C on 1-day UCS

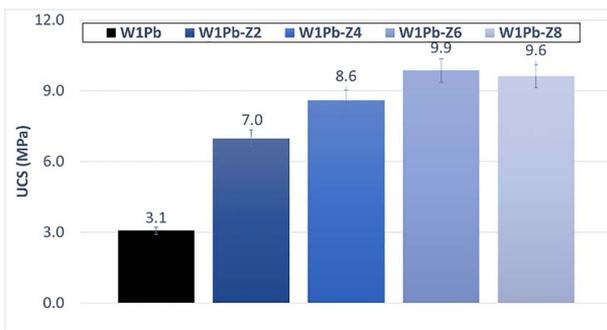


Fig. 4 The effect of chemical admixture Z on 1-day UCS

geopolymer recipes with higher water content than the 35% liquid-to-solid ratio could not set nor develop any reliable compressive strength within 1-day of heat curing at 70 °C. In addition, W1P (35% w/s, grey color bar) was much weaker than W1Pb (33% w/s, black color bar). The higher the water content, the lower the 1-day and 7-day UCS. W1Pb has almost triple the UCS value of W1P in agreement with the negative effect of water content on the geopolymer system in the literature [49].

Various chemical admixtures were added to the neat recipe to investigate each chemical admixture and its content on the neat one-part rock-based geopolymer recipe, W1Pb. A trend was obviously to be detected as the higher the content of chemical admixture the lower the 1-day UCS for chemical admixtures CaO, CaCO₃, and NaOH. Therefore, with higher chemical admixtures content, it has also a negative effect on 1-day UCS and early strength development.

In the case of the addition of NaOH Pellets, both partial and complete replacement of the accelerator solution by NaOH pellets had a severe decrease in 1-day UCS (Fig. 5). This effect was observed to lose down to two-thirds of the UCS of W1Pb. This could happen due to the substitution of the KOH accelerator solution with



Fig. 5 The effect of NaOH and KOH pellets on 1-day UCS

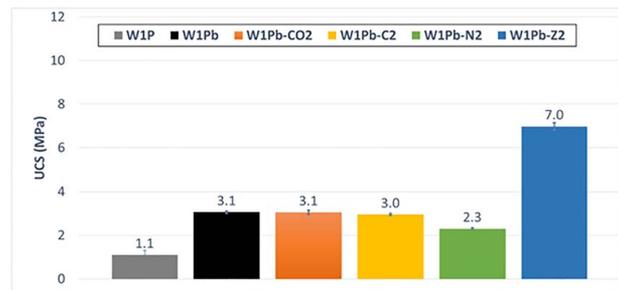


Fig. 6 The effect of various 0.14 wt% chemical admixtures on 1-day UCS

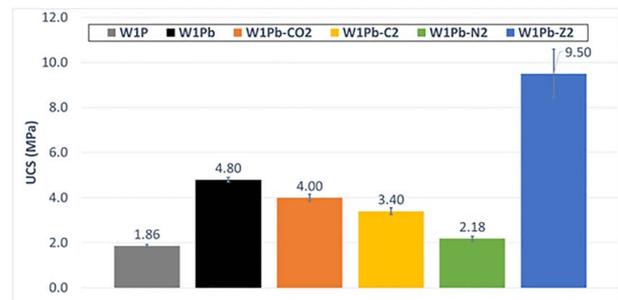


Fig. 7 The effect of various 0.14 wt% chemical admixtures on 7-day UCS

NaOH pellets by conserving the modulus ratio at 2.4. However, the rate of dilution of NaOH pellets is much slower than the utilization of any alkali solution with free ions. NaOH pellets need a longer time to be dissolved in the distilled water medium to be fully activated or so-called concentrated water for the 1P GP system. While the complete replacement of the KOH liquid accelerator by KOH pellets had a comparable 1-day UCS with the neat recipe W1Pb.

Unlike the other chemical admixtures, the utilization of chemical admixture Z has a weight content threshold to reach the highest 1-day UCS of 10 MPa after the addition of 0.86wt% Z to neat recipe W1Pb and then 1-day UCS decreased with higher Z content. A similar trend was also observed by Ali [50] and Zailan et al. [51].

Zinc oxide is partially soluble in an alkaline medium, but its solubility increases at elevated temperatures up to 100 °C [52]. It is an amphoteric oxide, formed by bonding the cation Zn⁺² with the anion O⁻². These elements can be presented in two possible structures: cubic and hexagonal as shown in Fig. 8.

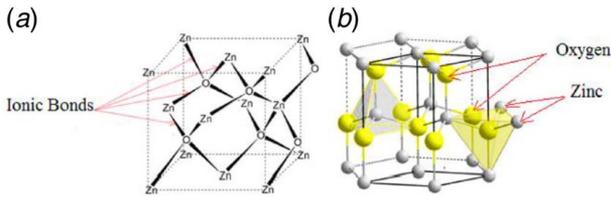


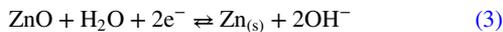
Fig. 8 Structures of ZnO: (a) cubic and (b) hexagonal [51]

ZnO can with MOH (M = K or Na) produce $ZnOH^+$, $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$ within the alkali pH range up to pH 14. At a high alkaline medium, the reaction between zinc oxide and alkali metal hydroxides (Am) produces two zincate-based anions: $MZn(OH)_3$ and $M_2Zn(OH)_4$. Figure 9 shows the chemical structure of Zincate $[Zn(OH)_3]^-$ polymeric anion. The presence of Zincate anions within the geopolymerization reaction may promote more favorable geopolymerization products



Other researchers observed not only a decrease in UCS at high concentrations of zinc oxide but also a threshold of the addition of zinc oxide to increase the compressive strength. Zinc oxide has been observed to play a role in the polycondensation phase by creating a more basic environment in the geopolymer system [51,53]. In a study by Zailan et al. [51], it was found that low concentrations of ZnO could fully control the formation of K(N)-A-S-H or C-A-S-H gels, from the complete geopolymerization reaction. It was also observed that more K(N)-A-S-H gel was formed than C-A-S-H gel during the geopolymerization process due to the low calcium content in the raw. However, it should be noted that these gel phases are indications of an incomplete geopolymerization reaction.

At higher concentrations of ZnO, UCS reduction could be due to the negative action of ZnO on the geopolymeric system, which might affect the condensation process and inhibit the formation of geopolymer gels [51]. The water molecules released during geopolymerization could introduce in reduction potential reaction with ZnO as shown in the following reversible chemical reaction [51]:



Therefore, the utilization of low concentrations of ZnO can improve the chemical kinetics of geopolymerization reaction to get higher and earlier strength development as observed for the addition of 0.14 wt% (equivalent to 25 mmol) up to 0.86 wt% (equivalent to 74 mmol) of ZnO to neat recipe W1Pb in Fig. 4.

3.2 Nondestructive Compressive Strength. According to API standards [48], the cement should harden after the well placement process within the first 12–24 h more than 3.5 MPa (500 psi) as a minimum requirement for UCA and UCS. In this study, 6.89 MPa (1000 psi) is considered an acceptable UCA and UCS of the given mix design for oil well cementing applications.

The given algorithms provided by UCA have been developed for OPC, and they are not reliable for estimating the strength

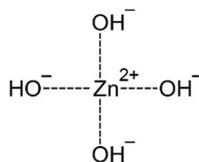


Fig. 9 Chemical structure of Zincate-based anion

Table 4 A polynomial equation for one-part rock-based geopolymers to estimate sonic strength from transit time data [11]

Mix design	Polynomial equation	R-Square value
W1P	$Y = 211.28X^2 - 6220X + 45677$	$R^2 = 96.12\%$

development of other materials such as one-part rock-based geopolymers [47,54].

The estimated sonic strengths showed that the development of algorithms to estimate the sonic strength from transit time is important. The speed of the compressional sonic wave is strongly affected by the chemistry of the under-investigated geopolymers [47].

A new empirical equation was developed by plotting the average compressive strength values versus measured transit time by the UCA equipment [11]. The equation is a polynomial equation for one-part rock-based geopolymers (Table 4).

Figures 10 and 11 present the sonic strength development curves based on the generated polynomial equation in Table 4.

Table 5 presents setting time data to reach 50 and 500 psi, besides, sonic strength data that has been observed after 1- and 7 days.

The estimated UCA data agree with the measured UCS values for the top candidate recipes for 1- and 7-day UCS as given in Figs. 6, 7 and 11. In Table 5, W1Pb-Z2 has the shortest time to reach 0.35 and 3.5 MPa. W1P with higher water content has the longest time to reach 0.35 and 3.5 MPa, which it was taking up to 19 days to reach 3.5 MPa. However, W1Pb was taking just one hour and six

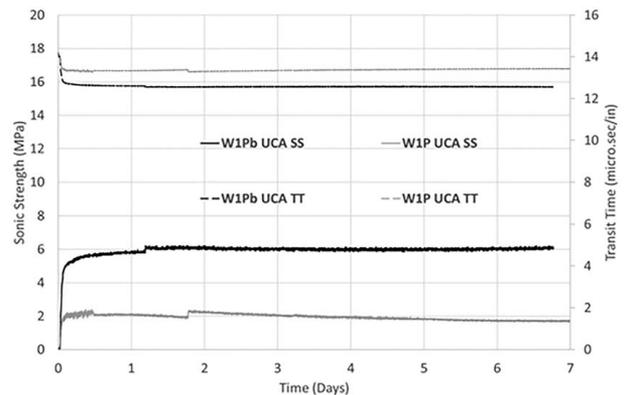


Fig. 10 UCA Data for the net recipe with two different water content, samples cured up to 7 days

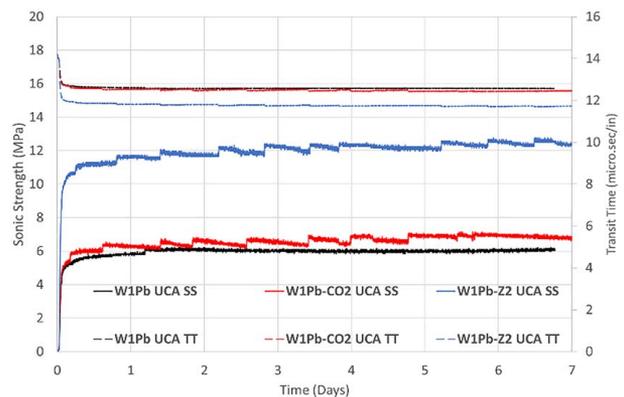


Fig. 11 UCA Data for samples containing 0.14 wt% chemical admixtures, cured up to 7 days

Table 5 Summary of UCA data for the selected 1P GP recipes

Mix design	Setting time (min) to 0.35 MPa (50 psi)	Setting time (min) to 3.5 MPa (500 psi)	SS (MPa) for 1 day	SS (MPa) for 7 days
W1P	46	27,540	1.68	2.11
W1Pb	40	66	5.85	6.10
W1Pb-CO2	38	60	6.22	6.74
W1Pb-Z2	37	47	11.55	12.76

minutes to reach the same sonic strength value. This shows and proves the severe effect of water content on geopolymers as shown in Fig. 10 and Table 5.

Furthermore, the estimated sonic strength for 1- and 7-day is slightly higher than the measured compressive strength for 1- and 7-day UCS. This could be due to the addition of pressure ca. 13.8 MPa while curing in UCA; however, the UCS samples were cured at ambient pressure [55].

3.3 Composition Analysis, X-Ray Diffraction. Generally, geopolymers are known to contain amorphous content, especially at low curing temperatures; however, the amorphous content is diminished at elevated curing temperatures [11,36,56–58]. Khalifeh et al. [57] studied the mineralogy of rock-based geopolymers synthesized by the use of potassium silicate solution as an activator. They found that quartz was a major phase, and albite and microcline were minor phases.

Figure 12 presents the peaks observed in the spectra of the given geopolymer precursors. It shows the phases originally found in the rock precursors of the granite, GGBFS, and microsilica, where granite has high crystalline content of up to 80%. On the other hand, GGBFS and microsilica are considered for their highly amorphous content and observable amorphous hump as given in Fig. 12. For GGBFS, akermanite crystalline mineral could be barely detected in addition to other trace minerals/contaminants. However, in the case of microsilica, there was not any detectable crystalline peak as shown in Fig. 12.

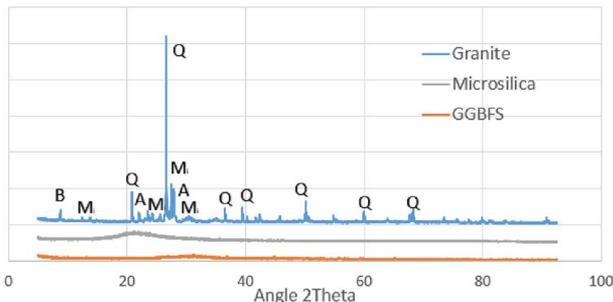


Fig. 12 Compositional analysis XRD for 1P GP precursor components

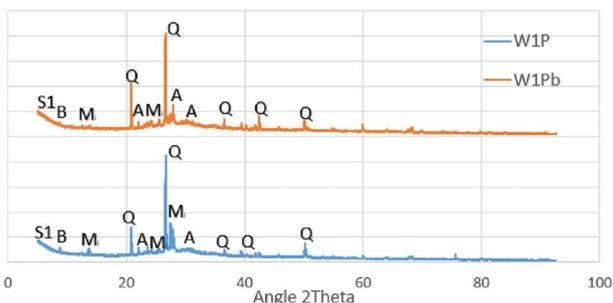


Fig. 13 XRD Compositional analysis for W1P versus W1Pb

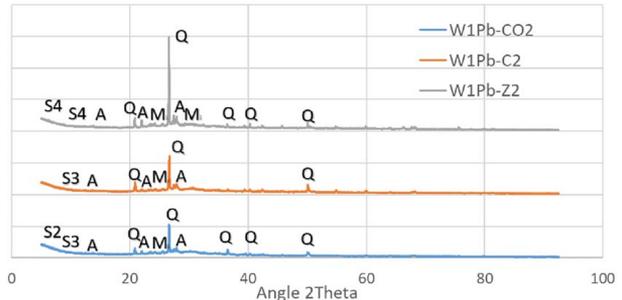


Fig. 14 XRD Compositional analysis for W1Pb* recipes

Granite main peaks correspond to quartz (SiO₂), microcline as an alkali feldspar (KAlSi₃O₈), and albite as a plagioclase feldspar (NaAlSi₃O₈). In addition, the precursor also contains biotite (K(Mg,Fe)3AlSi₃O₁₀(F,OH)2). However, Biotite mineral is not found or neglected in the spectra of any of the finished products as shown in Figs. 13 and 14. Table 6 indicates the computed crystalline and amorphous content for granite, the two neat recipes, and the developed recipes with chemical admixtures.

XRD Analysis shows similar patterns for the neat samples of the same original composition in Figs. 12 and 13. Figure 13 shows negligible major changes can be observed over the 7 days of curing, and no significant differences were found because of the differences in water content between W1P and W1Pb. Both neat recipes contain Quartz, Albite, Microcline, and tracers of Biotite and synthetic potassium aluminum-silicates hydrates (S1), but W1Pb has lower microcline and biotite content than W1P.

Figure 14 presents the differences in the compositional analysis of W1Pb with the 0.14wt% chemical additives of calcium oxide (CO), calcium carbonate (C), and zinc oxide (Z). These W1Pb* modified recipes also have Quartz, Albite and Microcline similar to the W1Pb neat, in addition to three synthetic crystals or hydrates. W1Pb-CO2 has two synthetic hydrates as tracers are Potassium–Sodium–Calcium–Aluminum–Silicate hydrates (S2) and Sodium–Calcium–Magnesium–Aluminum–Silicate hydrates (S3). W1Pb-C2 has tracers of synthetic Sodium–Calcium–Magnesium–Aluminum–Silicate hydrate (S3) only. While W1Pb-Z2 has just tracers of Potassium Zinc Aluminum–Silicate hydrates (S4).

Two trends were visible in the geopolymer samples. Over time, the composition changes slightly, and the presence of feldspar reduces in agreement with [11,36,56,57] and the presence of synthetic hydrates as a function of each added chemical admixture

Table 6 Degree of crystallinity analysis for granite and the selected recipes

Mix design	Crystallinity (%)	Amorphosity (%)
Granite	79.9	20.1
W1P	52.1	47.9
W1Pb	51.7	48.3
W1Pb-CO2	53.2	46.8
W1Pb-C2	50.1	49.9
W1Pb-Z2	53.0	47.0

even if as tracers. For W1P and W1Pb cured at 70 °C, there were little peaks of feldspar crystals after the 7 days of curing (Fig. 13). Similarly, W1Pb* recipes also have little trace of feldspar crystals after 7 days of curing, while the main peak of Biotite seemed to be diminished over the 7 days of heat curing (Fig. 14).

Therefore, this can suggest a chemical reaction between the geopolymer, chemical admixtures, and the feldspars (Albite and Microcline) present in the precursor. The absence of biotite in all products may also suggest a chemical reaction between the mixtures and biotite, but this absence can also be related to a lesser amount of biotite relative to that total in the final mix, thus making it difficult to differentiate in the XRD spectra.

The results also indicate that different types of feldspar react differently with and without the chemical admixtures put into the geopolymers. In addition, three new synthetic hydrates were observed after the addition of the investigated chemical admixtures (CO, C, and Z).

Further examinations and future studies are still needed to fully understand these complex chemical investigations and their economic feasibility. These studies should investigate and verify the geopolymerization process of these one-part geopolymer recipes, especially after adding ZnO as a strength booster. This investigation can be done by studying each stage of the geopolymerization reaction and by integrating other physical and chemical characterizations.

4 Conclusion

The development of an applicable mix design for one-part geopolymers is crucial to fit for offshore oil well cementing applications. The investigated geopolymers were heat-cured rock-based one-part recipes. They can be eligible for the development of short-term mechanical and chemical properties of cementing material. The developed W1Pb-Z recipes have the potential to be utilized in well construction and well abandonment applications. Furthermore, the higher water content in the one-part rock-based geopolymer system negatively affected the early strength development and setting time. Moreover, the higher the concentration of the given chemical admixtures, the lower the 1-day strength development. The top candidate recipes were having lower water content and especially with lower concentration of ZnO chemical admixture, as ZnO might have a role in the polycondensation phase in the geopolymer system. This can be due to the formation of the polymeric anions of zincate. Thus, ZnO can be considered an early strength development booster. Further investigations are still needed to fully understand the complexity behind the one-part rock-based geopolymerization process.

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Conflict of Interest

There are no conflicts of interest.

Data Availability Statement

The data sets generated and supporting the findings of this article are obtainable from the corresponding author upon reasonable request.

Nomenclature

Acronyms

A	=	albite
C	=	calcium carbonate
CO	=	calcium oxide
CuK α	=	copper k-alpha radiation
FA	=	fly ash
GGBFS	=	ground granulated blast furnace slag
K	=	potassium
M	=	alkali metal
Mi	=	microcline
Mmol	=	millimoles
MPa	=	mega Pascal
MR	=	modulus ratio
N	=	sodium hydroxide
Na	=	sodium
OPC	=	Ordinary Portland Cement
P&A	=	plugging and abandonment
Q	=	quartz
S1	=	synthetic potassium aluminum silicates hydrates
S2	=	synthetic potassium sodium calcium aluminum silicate hydrates
S3	=	synthetic sodium calcium magnesium aluminum silicate hydrates
S4	=	synthetic potassium zinc aluminum silicate hydrates
SS	=	sonic strength
TT	=	transient time
UCA	=	ultrasonic cement analyzer
UCS	=	uniaxial compressive strength
W1Pb*	=	W1Pb modified recipes with 0.14wt% chemical admixtures
W1Pc	=	“Just Add Water” rock-based geopolymer mix design
XRD	=	X-ray diffraction
Z	=	zinc oxide
2 θ	=	two theta angle
1P GP	=	one-part geopolymer

References

- [1] Cement industry News and Events From World Cement With the Latest News Updates. World Cement. (n.d.). <https://www.worldcement.com/>
- [2] IEA. (n.d.). Net Zero Emissions by 2050 Scenario (NZE)—Global Energy and Climate Model—Analysis. IEA. <https://www.iea.org/reports/global-energy-and-climate-model/net-zero-emissions-by-2050-scenario-nze>
- [3] Liu, Y., and Rui, Z., 2022, “A Storage-Driven CO₂ EOR for a net-Zero Emission Target,” *Engineering*, **18**, pp. 79–87.
- [4] Andrew, R., 2021, Review of “Cdiac-ff: Global and National CO₂ emissions From Fossil Fuel Combustion and Cement Manufacture: 1751-2017”, ESSD-2020-337.
- [5] Damtoft, J. S., Lukasik, J., Herfort, D., Sorrentino, D., and Gartner, E. M., 2008, “Sustainable Development and Climate Change Initiatives,” *Cem. Concr. Res.*, **38**(2), pp. 115–127.
- [6] McLellan, B. C., Williams, R. P., Lay, J., van Riessen, A., and Corder, G. D., 2011, “Costs and Carbon Emissions for Geopolymer Pastes in Comparison to Ordinary Portland Cement,” *J. Cleaner Prod.*, **19**(9–10), pp. 1080–1090.
- [7] Provis, J. L., and Van Deventer, J., 2009, *Geopolymers: Structures, Processing, Properties and Industrial Applications*, Woodhead, Oxford.
- [8] Duxson, P., Fernández-Jiménez, A., Provis, J. L., Lukey, G. C., Palomo, A., and van Deventer, J. S., 2006, “Geopolymer Technology: The Current State of the Art,” *J. Mater. Sci.*, **42**(9), pp. 2917–2933.
- [9] Duxson, P., and Provis, J. L., 2008, “Designing Precursors for Geopolymer Cements,” *J. Am. Ceram. Soc.*, **91**(12), pp. 3864–3869.
- [10] Singh, B., Ishwarya, G., Gupta, M., and Bhattacharyya, S., 2015, “Geopolymer Concrete: A Review of Some Recent Developments,” *Const. Build. Mater.*, **85**, pp. 78–90.
- [11] Omran, M., and Khalifeh, M., 2022, “Development of Low Carbon Dioxide Intensive Rock-Based Geopolymers for Well Cementing Applications—One-Part Geopolymer,” Proceedings of the ASME 2022 41st International Conference on Ocean, Offshore and Arctic Engineering. Volume 10: Petroleum Technology, Hamburg, Germany, June 5–10, 2022. p. V010T11A043.
- [12] Sagoe-Crentsil, K., Brown, T., and Taylor, A., 2013, “Drying Shrinkage and Creep Performance of Geopolymer Concrete,” *J. Sustain. Cem. Based Mater.*, **2**(1), pp. 35–42.
- [13] Bakri, A. M., Kamarudin, H., Binhusain, M., Nizar, I. K., Rafiza, A. R., and Zarina, Y., 2013, “Comparison of Geopolymer Fly Ash and Ordinary Portland Cement to the Strength of Concrete,” *Adv. Sci. Lett.*, **19**(12), pp. 3592–3595.

- [14] Shi, C., Shi, Z., Hu, X., Zhao, R., and Chong, L., 2015, "A Review on Alkali-Aggregate Reactions in Alkali-Activated Mortars/Concretes Made With Alkali-Reactive Aggregates," *Mater. Struct.*, **48**(3), pp. 621–628.
- [15] Mehta, A., and Siddique, R., 2016, "An Overview of Geopolymers Derived From Industrial By-Products," *Construct. Build. Mater.*, **127**, pp. 183–198.
- [16] Khalifeh, M., Saasen, A., Larsen, H. B., and Hodne, H., 2017, "Development and Characterization of Norite-Based Cementitious Binder From an Ilmenite Mine Waste Stream," *Adv. Mater. Sci. Eng.*, **2017**, pp. 1–7.
- [17] Van Deventer, J. S. J., Provis, J. L., and Duxson, P., 2012, "Technical and Commercial Progress in the Adoption of Geopolymer Cement," *Miner. Eng.*, **29**, pp. 89–104.
- [18] Kühl, H., 1908, Slag Cement and Process Making the Same, US Patent No. 900,939.
- [19] Glukhovskiy, V. D., 1959, Soil Silicates. Gostroiizdat Publish, Kiev, 1959.
- [20] Krivenko, P. V., 1986, "Synthesis of Cementitious Materials of the Me₂O-MeO-Me₂O₃-SiO₂-H₂O System With Required Properties," D.Sc. (Eng) thesis, KISI Public, Kiev.
- [21] Davidovits, J., 1991, "Geopolymers," *J. Therm. Anal.*, **37**(8), pp. 1633–1656.
- [22] Palomo, A., Blanco-Varela, M. T., Granizo, M. L., Puertas, F., Vazquez, T., and Grutzeck, M. W., 1999, "Chemical Stability of Cementitious Materials Based on Metakaolin," *Cem. Concr. Res.*, **29**(7), pp. 997–1004.
- [23] Khale, D., and Chaudhary, R., 2007, "Mechanism of Geopolymerization and Factors Influencing Its Development: A Review," *J. Mater. Sci.*, **42**(3), pp. 729–746.
- [24] Pacheco-Torgal, F., Castro-Gomes, J., and Jalali, S., 2008, "Alkali-activated Binders: A Review," *Construct. Build. Mater.*, **22**(7), pp. 1305–1314.
- [25] Pacheco-Torgal, F., Castro-Gomes, J., and Jalali, S., 2008, "Alkali-Activated Binders: A REVIEW. Part 2. About Materials and Binders Manufacture," *Construct. Build. Mater.*, **22**(7), pp. 1315–1322.
- [26] Al Bakri, A. M., Kamarudin, H., Bnhussain, M., Nizar, I. K., and Mastura, W., 2011, "Mechanism and Chemical Reaction of Fly Ash Geopolymer Cement: A Review," *J. Asian Sci. Res.*, **1**(5), pp. 247–253. Retrieved from <https://archive.aessweb.com/index.php/5003/article/view/3292>
- [27] API, R.P 10B-2, 2013, *Recommended Practice for Testing Well Cements*, API, Washington, DC.
- [28] Luukkonen, T., Abdollahnejad, Z., Ylioniemi, J., Kinnunen, P., and Illikainen, M., 2018, "One-Part ALKALI-ACTIVATED Materials: A Review," *Cem. Concr. Res.*, **103**, pp. 21–34.
- [29] Hos, J. P., McCormick, P. G., and Byrne, L. T., 2002, "Investigation of a Synthetic Aluminosilicate Inorganic Polymer," *J. Mater. Sci.*, **37**, pp. 2311–2316.
- [30] Wang, D., and Chen, Z., 1997, "On Predicting Compressive Strengths of Mortars With Ternary Blends of Cement, Ggbfs and Fly Ash," *Cem. Concr. Res.*, **27**(4), pp. 487–493.
- [31] Nugteren, H. W., 2007, "Coal Fly Ash: From Waste to Industrial Product," *Part. Syst. Charact.*, **24**(1), pp. 49–55.
- [32] Puertas, F., Martínez-Ramírez, S., Alonso, S., and Vázquez, T., 2000, "Alkali-Activated Fly Ash/Slag Cements," *Cem. Concr. Res.*, **30**(10), pp. 1625–1632.
- [33] Li, C., Sun, H., and Li, L., 2010, "A Review: The Comparison Between Alkali-Activated Slag (si+ca) and Metakaolin (Si+Al) Cements," *Cem. Concr. Res.*, **40**(9), pp. 1341–1349.
- [34] Rahier, H., Van Mele, B., and Wastiels, J., 1996, "Low-Temperature Synthesized Aluminosilicate Glasses," *J. Mater. Sci.*, **31**(1), pp. 80–85.
- [35] Provis, J. L., 2018, "Alkali-Activated Materials," *Cem. Concr. Res.*, **114**, pp. 40–48.
- [36] Omran, M., Khalifeh, M., and Hjelm, S., 2022, Role of Zeta Potential on Rheology of One-Part Geopolymer Slurries-Influence of Superplasticizers. I: Annual Transactions the Nordic Rheology Society. ISBN 978-82-692721-2-3. s.15-22.
- [37] Purdon, A. O., 1940, "The Action of Alkalis on Blast-Furnace Slag," *J. Soc. Chem. Ind.*
- [38] Heitzmann, R. F., Fitzgerald, M., and Sawyer, J. L., 1987, Mineral Binder and Compositions Employing the Same, Mineral Binder and Compositions Employing the Same. US Patent No. 4,642,137.
- [39] Schwarz, W., and Lerat, A., 1994, Tectoaluminosilicate Cement and a Process for Its Manufacture, Tectoaluminosilicate Cement and a Process for Its Manufacture. U.S. Patent No. 5,372,640.
- [40] Davidovits, J., 1994, Method for Obtaining a Geopolymeric Binder Allowing to Stabilize, Solidify and Consolidate Toxic or Waste Materials, Method for Obtaining a Geopolymeric Binder Allowing to Stabilize, Solidify and Consolidate Toxic or Waste Materials. U.S. Patent No. 5,349,118.
- [41] Glasby, T., Day, J., Genrich, R., and Aldred, J., 2015, "EFC Geopolymer Concrete Aircraft Pavements at Brisbane West Wellcamp Airport," Proceedings of the 27th Biennial National Conference of the Concrete Institute of Australia in Conjunction With the 69th RILEM Week, Melbourne, Australia, Aug. 30–Sept. 2, Concrete Institute of Australia, Sydney.
- [42] Palomo, A., Fernández Jiménez, A., López Hombrados, C., and Lleyda, J. L., 2007, "Railway Sleepers Made of Alkali Activated fly ash Concrete," *Rev. Ing. De Constr.*, **22**(2).
- [43] Norsok, D., 2013, Well Integrity in Drilling and Well Operations. Standards Norway, Rev. 4, Lysaker, Norway.
- [44] Haghighat-Nejad, F., 2019, *Flexible Geopolymer for Oil and Gas Well Cementing: An Experimental Study*, University of Stavanger, Norway.
- [45] Khalifeh, M., 2016, "Materials for Optimized P&A Performance: Potential Utilization of Geopolymers," PhD thesis UiS, University of Stavanger, Norway.
- [46] API Spec 10A, 2015, *Specification for Cements and Materials for Well Cementing*, 23rd ed., American Petroleum Institute, Washington, DC.
- [47] Kamali, M., Khalifeh, M., Saasen, A., and Delabroy, L., 2020, "Materials for Well Integrity: Characterization of Short-Term Mechanical Properties," *Proceedings of the ASME 2020 39th International Conference on Ocean, Offshore and Arctic Engineering. Volume 11: Petroleum Technology*, Virtual, Online, Aug. 3–7, ASME, p. V011T11A035.
- [48] API RP 10B-2, 2019, *Recommended Practice for Testing Well Cements*, American Petroleum Institute, Washington, DC.
- [49] Park, S., and Pour-Ghaz, M., 2018, "What Is the Role of Water in the Geopolymerization of Metakaolin?," *Constr. Build. Mater.*, **182**, pp. 360–370.
- [50] Pathak, A., 2017, "Effect of Zinc Oxide Nanoparticle on Compressive Strength and Durability of Concrete," *Int. J. Res. Appl. Sci. Eng. Technol.*, **V**(VIII), pp. 683–687.
- [51] Zailan, S. N., Bouaissi, A., Mahmed, N., and Abdullah, M. M., 2019, "Influence of ZnO Nanoparticles on Mechanical Properties and Photocatalytic Activity of Self-Cleaning ZnO-Based Geopolymer Paste," *J. Inorg. Organomet. Polym. Mater.*, **30**(6), pp. 2007–2016.
- [52] Chen, A.-l., Xu, D., Chen, X.-y., Zhang, W.-y., and Liu, X.-h., 2012, "Measurements of Zinc Oxide Solubility in Sodium Hydroxide Solution From 25 to 100 °C," *Trans. Nonferr. Metals Soc. China*, **22**(6), pp. 1513–1516.
- [53] Nivethitha, D., and Dharmar, S., 2016, "Influence of Zinc Oxide Nanoparticle on Strength and Durability of Cement Mortar," *Int. J. Earth Sci. Eng.*, **9**(3), pp. 175–181.
- [54] Khalifeh, M., Saasen, A., and Vrålstad, T., 2014, "Potential Utilization of Geopolymers in Plug and Abandonment Operations," Proceedings of the SPE Bergen One Day Seminar, Bergen, Norway, Apr. 2.
- [55] Scherer, G. W., Funkhouser, G. P., and Peethamparan, S., 2010, "Effect of Pressure on Early Hydration of Class H and White Cement," *Cem. Concr. Res.*, **40**(6), pp. 845–850.
- [56] Chamssine, F., Khalifeh, M., Eid, E., Minde, M. W., and Saasen, A., 2021, "Effects of Temperature and Chemical Admixtures on the Properties of Rock-Based Geopolymers Designed for Zonal Isolation and Well Abandonment," *Proceedings of the ASME 2021 40th International Conference on Ocean, Offshore and Arctic Engineering. Volume 10: Petroleum Technology*, Virtual, Online, June 21–30, ASME, p. V010T11A031.
- [57] Khalifeh, M., Saasen, A., Vrålstad, T., Larsen, H. B., and Hodne, H., 2016, "Experimental Study on the Synthesis and Characterization of Aplite Rock-Based Geopolymers," *J. Sustain. Cem. Based Mater.*, **5**(4), pp. 233–246.
- [58] Omran, M., Khalifeh, M., and Saasen, A., 2022, "Influence of Activators and Admixtures on Rheology of Geopolymer Slurries for Well Cementing Applications," *Proceedings of the SPE Asia Pacific Oil & Gas Conference and Exhibition*, Adelaide, Australia, Oct. 17–19.