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Alkali-activated aluminosilicate sealing system for deep high-temperature well applications

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\textbf{A B S T R A C T}

This study proposes potential replacement for the Portland-based cement, which is a common sealant used in deep high-temperature geothermal wellbore completions. The experimental laboratory studies were focussed on alkali-activated aluminosilicates. It was proven, that the so-called, geopolymer-based sealing systems exhibit high compressive and flexural strength at elevated temperatures, good resistance towards thermal cyclic loading, high ductility, acid insensitivity, and improved water permeability. Additionally, alkali-activated aluminosilicate sealing systems are economically feasible and their CO\textsubscript{2} emission, during the manufacturing process, is significantly lower in comparison with the conventional Portland-based cement types, making them an environmentally friendly option for deep wellbore completions in unconventional high-temperature geothermal systems.

1. Introduction

Recent studies have proven, that productivity of a conventional high-temperature geothermal well will be increased by a factor of ten if supercritical fluids, with temperature and pressure conditions being equal or exceeding the critical point, would have been extracted (Fridleifsson et al., 2005, 2014a, 2014b). With this approach, only one deep, so-called, “supercritical” well, instead of multiple conventional high-temperature ones can be drilled to achieve similar productivity. To be able to produce from such unconventional high-temperature geothermal recourse, much deeper depths have to be penetrated. Based on the assumption that the formation temperature is represented by a boiling point temperature-depth (BPTD) curve with boiling conditions starting at the well’s surface, which is a common assumption for well design in high-temperature hydrothermal systems, and reservoir fluids being pure water only one has to drill to a depth of approximately 3500 m (Fig. 1) to penetrate supercritical resources. It is, however, a rather unusual case, that reservoir fluid is pure water only. Often, reservoir fluids have elevated salt content (e.g., Reykjanes geothermal field in Iceland or Salton Sea geothermal field in the USA). In such cases, the critical point is achieved at much greater depths (e.g., approximately 5300 m for the case of seawater) (Fig. 1). The longevity of geothermal production from a single wellbore drilled into the supercritical resource depends significantly on the applied drilling and wellbore completion technologies (Kruszewski and Wittig, 2018). Deep and high-temperature drilling projects in countries such as Iceland, Italy, Kenya, Japan, Greece, the USA, or Mexico have all reached critical temperatures and, in many cases encountered highly corrosive and hostile reservoir fluids. Such extreme reservoir conditions promoted significant damages to the casing material, cement sheath, surface equipment, and eventually led to serious well failures or, in some cases, to total well abandonment. These drilling campaigns created an acute need for improvements of the currently used drilling and wellbore completion technologies exploring unconventional high-temperature geothermal resources (Kruszewski and Wittig, 2018).

Cementitious mixtures based on the Ordinary Portland Cement (OPC) and high silica flour content are primarily used in completions of petroleum and geothermal wells. While such mixtures might be sufficient for ordinary depths and reservoir temperatures, extreme and more severe downhole conditions, being encountered more often in deep geothermal wells at various locations worldwide, create need for significant improvements in wellbore sealant materials and their placement techniques (Kruszewski and Wittig, 2018; Kruszewski et al., 2019). Currently used sealing systems for geothermal wells, based exclusively on Portland cement systems, are not designed to withstand extreme temperatures going beyond the critical point of the reservoir fluid (NZS 2403, 2015). Not only the phenomenon of strength retrogression (Brezerra et al., 2011) but also the thermal expansion and...
shrinkage at high temperatures as well as thermal cyclic loading (during e.g., geothermal fluid production or wellbore quenching) (Kaldal et al., 2015) cause challenges to the binding matrix of the Portland-based sealing systems. Samples acquired from supercritical drilling ventures have proven that the pH level of reservoir fluids will be likely acidic (Ármannsson et al., 2014) and aggressive to the sealant, if direct contact between both will occur. The same goes for the operation of acid stimulation, if contact between wellbore cement and the stimulation fluid occurs.

Since decades the geothermal industry uses Portland-based cement with a high amount of silica flour and auxiliary additives in almost all deep wellbore completions. Such systems, until recently and up to certain temperature limits, proved rather good and long-term performance. The recent failures of both Iceland Deep Drilling Project (IDDP) wells, prove that at more extreme temperature conditions conventional wellbore completion materials and methods are insufficient. One of the promising alternative sealing systems for high-temperature geothermal wells are thought to be the non-Portland sealing mixtures. These sealing systems are still relatively unknown in the drilling industry and practically not used in completions of deep geothermal wells. This is primarily due to the lack of information on their long-term performance as well as behaviour in extreme downhole conditions. In the recent Venelle-2 drilling campaign in the Larderello geothermal field (Italy), where supercritical conditions of geothermal brine were targeted, the formed C-S-H phase, responsible for the strength and stability of the hardened cement slurry at ordinary temperatures. At elevated temperatures, common in geothermal reservoirs, C-S-H phases are subjected to the metamorphism processes, which result in rapid deterioration of strength properties and an increase in water permeability (strength retrogression) (Nelson et al., 2006). Portland cement sealing systems used for annular cement in a wellbore are designed to perform at a temperature range between conditions below freezing point up to temperatures of 350 °C and in the pressure, conditions ranging from ambient conditions up to 200 MPa. In addition to the ever-changing temperatures and pressures during the lifetime of a wellbore, cement is often designed to withstand over-pressurized, porous formations, and corrosive reservoir fluids. To accommodate such conditions, auxiliary cement additives are used. They modify the wet and hardened cement behaviour, allowing for successful slurry placement, rapid strength development, and effective zonal isolation (Nelson et al., 2006). In sealing systems used in deep high-temperature wells, high quantities of silica flour are added to the base Portland cement mixture, which is mainly to prevent early strength retrogression. Silica flour consists of approximately 98% silicon dioxide (SiO2) and it does not interfere with the hydration process under atmospheric conditions. Retarder is often added to the cement mixture to prolong its workability and pumpability during placement in the borehole, and to prevent its premature setting in the cementing string. This is especially the case, during cementation of long casing strings when the cement has to travel long distances to reach the casing bottom and/or when high temperatures are expected in-situ. A variety of different types of retarders are used in the geothermal industry. In general, retarder intervenes strongly with the chemical-mineralogical reactions of the cement hydration with the intervention proceeding differently depending on the type of retarder used.

Alkali-activated aluminosilicates (in some sources described as geopolymers, inorganic polymers, mineral polymers, or zeocements) sealing systems consist of a base material composed of an aluminium silicate combined with an alkaline solution. In the instance of this paper, a geopolymer always refers to a polymer component based on aluminium silicates and should not be confused with organic polymers of any other origin. Aluminium silicate sources can be natural, such as metakaolin, or industrially produced. The merging of the alkaline solution initiates the formation of a gel-like matrix consisting of different oligomeric units, referred to as “polysialates”. Such units form a chain of structured polymers containing Si⁴⁺ and Al³⁺. The main structure of the formed oligomers consists of quadratic-planar shaped tetrahedrons with a coordination number of 4. The coordination number, often referred to as ligancy describes the number of ions, molecules, or atoms that are the closest neighbour in a compound or crystalline structure. The molecular formula of a formed gel always shows the following structure (Duxson et al., 2005)

$$M_p[\left(\text{SiO}_2\right)_x - \text{AlO}_2\right]_y \cdot n\text{H}_2\text{O}$$  \hspace{1cm} (1)

where, $M$ is a monovalent alkali metal cation such as Na⁺ or K⁺, $p$ is the degree of polycondensation, and $x$ is the stage of the sialate (e.g., $x$ of 2 describes poly-sialate-siloxo with a structure of $\text{-Si-O-Al-O-Si-O}$) (Rangan and Hardjito, 2005). As can be seen from Eq. 1, there can be...
several SiO₂ molecules associated with one AlO₂ molecule. The relation of Si to Al has therefore great influence on the resulting structure. Increasing the Si amount leads to more complex amorphous structures increasing the stability of the gel-phase and determining properties of the resulting material (Davidovits, 1991).

2. Materials

Comparative analysis of a proprietary geopolymer sealing system (Table 1) with a conventional Portland-based cement system, representative of a cement blend type used within the Los Humeros geothermal field (LHGF), one of the four biggest geothermal fields in Mexico, for primary cementing of productive casing strings (Table 2), was carried out.

Portland cement type used in this case study was CEM I 52.5 R NA. Here, CEM I indicates Portland type cement with up to 5 % of minor additional constituents, 52.5 describes compressive strength (in MPa) achieved after 28 days of cement curing, R indicates rapid cement setting, whereas NA signifies low alkali cement type. Based on the manufacturer’s specification silica flour and silica sand, used in this study, have a bulk density of 2650 kg/m³, with < 0.02 M.-% of impurities. For the case of the silica flour, 100 M.-% passes a sieve of 0.2 mm, 99 M.-% passes a sieve of 0.125 mm, 98 M.-% passes a sieve of 0.063 mm. For the case of the silica sand, 100 M.-% passes a sieve of 0.5 mm, 44 M.-% passes a sieve of 0.25 mm, and 1 M.-% passes a sieve of 0.125 mm. An inorganic phosphate-based type cement retarder available under the market name of Centrament Retard 360 was added to the conventional Portland cement mixture. This type of retarder usually produces higher final cement strengths. Based on the manufacturer’s specification, retarder has a density of 1210 ± 30 kg/m³, whereas the maximum chloride content to < 0.1 M.-%, and the maximum alkaline content to < 12 M.-%.

The hardener mixture of the geopolymer blend, designed especially for this study, consists of an aqueous, eight molar solution of sodium hydroxide (NaOH) and soda water glass (Na₂SiO₃), composed of 26.3 % silicate and 7.9 % sodium oxide. The composition of the hardener mixture included 18.0 kg on 1 m³ of geopolymer blend of NaOH, 67.8 kg on 1 m³ of geopolymer blend of Na₂SiO₃, and 188 kg on 1 m³ geopolymer blend of water. The combination of the hardener solution and the aluminum silicate leads to the gel formation processes, which initiates the curing processes. In this study, the industrial aluminium silicate fly ash was used as a base material for creating a sealing system for a potential application in a high-temperature geothermal well. This fly ash is a by-product of hard coal combustion, having, therefore, a positive environmental footprint. The fly ash under the market name of EFA Füller HP was used in this study. According to the specification of the manufacturer, the hard coal fly ash is composed of > 25 M.-% of reactive SiO₂, loss of ignition (LOI) of < 5 M.-%, grain fraction (> 45 μm) of 20 ± 10 M.-%, bulk density of 1110 kg/m³, and grain density of 2320 ± 200 kg/m³. To improve the performance and workability of a fresh geopolymer sealant, superplasticizer, under a market name of Leiqual 89 was added to the mixture. The raw material source of the superplasticizer is melamine resin. The used superplasticizer is of liquid consistency and is soluble in water. The density of the superplasticizer amounts to 1170 ± 30 kg/m³ with the maximum chloride content of < 0.1 M.-%, and pH ranging between 8.5 and 11.5. It is worth mentioning that performance of superplasticizers at elevated temperatures may be substantially impeded. However, it is assumed that during sealant placement in a deep geothermal borehole, the reservoir will be substantially cooled down due to the fluid circulation during drilling. With this assumption, we don’t expect exposure of the sealant to temperatures higher than 100 °C during placement in the borehole. To improve the strength and elastic properties of both sealing systems, different types of fibres were considered in this study. Conventional fibres types, commonly used in the concrete industry, include glass fibres, polymer fibres, steel fibres, stainless-steel fibres, and carbon fibres. The first four fibres types were investigated in this study.

3. Methods

The mixing process is of major importance for the fresh and early age properties of both sealing systems. Adjustable factors include mixing sequence, ambient temperature, aggregate temperature, mixing time, mixing speed, mixing volume, and mixer type (e.g., different mixing paddles). The mortar mixer ToniMIX was used for mixing of both sealants following the ASTM C305−14 standard (2014).

In the first step of Portland cement mixing, needed water and retarder were brought into contact in a separate container. The mixture was then poured into a mixing bowl. The cement was added within 30 s to initiate the hydration reactions. The mixer started working on a low mixing speed for 30 s. Within the first 30 s of mixing the optional fibres were added to the mixture. After initial mixing, speed was set to fast for another 30 s. Rim and bottom of the mixing bowl were scraped to make sure that all of the ingredients are evenly distributed within the mixture and no residues are left in the mixing bowl. After the scraping procedure, the mixer speed was set to fast for another 60 seconds. This routine was applied to every Portland cement mixture, assuring reasonably consistent results.

For geopolymers, the same time steps of mixing routine were applied. First, the hardener solution and superplasticizer were poured into the mixing bowl. Within 30 s, fly ash was added, and the chemical reaction was initiated. Mixing on the low speed was started for another 30 s. Within this time, silica sand was added to the mixture. The optional fibres were added during the first 30 s of the mixing procedure. After the initial mixing period, speed was set to fast for another 30 s. Following the fast speed mixing, the bowl rim and its bottom were scraped for 30 s to assure even distribution of all ingredients and avoid sticking. Afterward mixing on the fast speed was continued for another 60 s.

To imitate the curing of the sealant mixture in a borehole environment, three different curing conditions variants of the prepared Portland and non-Portland geopolymer samples were selected (Table 3). The first curing condition assumed ambient temperature and pressure conditions of the cementing laboratory. It is the least representative curing condition of the borehole conditions, as an annular sealant in any deep high-temperature borehole will never be subjected to atmospheric ambient conditions. The second variant assumed the curing process in an oven (Fig. 2) at temperatures ranging between 80 °C and 220 °C, representing curing conditions of a deep geothermal environment.

### Table 1
Alkali-activated aluminosilicate (geopolymer) sealant composition.

| Components          | Quantity, kg/m³ | Bulk density, kg/m³ | Volume, m³ |
|---------------------|-----------------|---------------------|------------|
| Silica sand         | 1052            | 2650                | 0.397      |
| Fly ash             | 639             | 2320                | 0.275      |
| Sodium hydroxide    | 78              | 1320                | 0.059      |
| Sodium silicate     | 196             | 1700                | 0.115      |
| Superplasticizer    | 12              | 1170                | 0.010      |
| Air-filled voids    | –               | –                   | 0.143      |

### Table 2
Ordinary Portland Cement (OPC) blend composition.

| Components          | Quantity, kg/m³ | Bulk density, kg/m³ | Volume, m³ |
|---------------------|-----------------|---------------------|------------|
| CEM I 52.5 R NA     | 912             | 3100                | 0.294      |
| Silica flour        | 365             | 2650                | 0.138      |
| Cement retarder     | 9               | 1210                | 0.008      |
| Air-filled voids    | –               | –                   | 0.020      |
| Water               | 540             | 1000                | 0.540      |
well, and ambient pressures. The inside environment of the oven was not controlled in other means than temperature. Therefore, low moisture content can be assumed. The different temperatures applied were 80, 100, 120, 160, 180, 200, and 220 °C. This represents extreme conditions for a cement curing processes under the absence of water and extremely high reservoir temperatures, imitating severe dehydration (during e.g., total fluid losses or “blind” drilling). Additionally, an oven is being used to carry out a thermal cyclic loading resistance test (only temperature controlled). There, samples were exposed to the temperature of 400 °C and then being rapidly cooled in a water bath with the temperature of 20 °C imitating an undesirable case of wellbore quenching, which may potentially occur during drilling or fluid production. One cycle in the thermal cyclic loading experiment consisted of 10 min exposure to 400 °C followed by 5 min of cooldown in the 20 °C water bath. The duration of sealant curing process in an oven ranged between 1 and 7 days.

The most representative conditions of annular sealant curing are hydrothermal conditions with applied elevated temperatures and moderate pressures. Such conditions are the most representative of the conditions sealant will be exposed to in the borehole environment. The reactor was used to imitate hydrothermal sealant curing. There samples were exposed to high temperatures of up 200 °C. The vapour pressure was adjusted to 1.55 MPa (the highest possible conditions achieved in this type of reactor in the laboratory conditions) preventing any potential water evaporation (Fig. 2). The duration of OPC and geopolymer sealing system samples curing in the reactor ranged between 1 and 7 days. Due to the time-consuming preparation and process of carrying out of the experiment in the reactor, only one measurement for compressive and flexural strength for each sealant type was allowed.

Beside withstanding extremely high static reservoir temperatures and/or temperatures resulting from e.g. fluid production, the annular sealant has to often withstand aggressive and acidic working or production fluids. The direct contact of the cement with acidic fluids may occur during e.g., stimulation with acids, which aims at increasing permeability of the reservoir, or in the case of a reservoir fluid flow through deboned sections at the casing-cement or rock-cement interfaces (Kruszewski et al., 2019). To test the acid-resistance of the OPC and geopolymer samples, an “acid bath” experimental test was developed (Fig. 3). Cured samples of each blend were inserted into the 6 % solution of the hydrogen chloride (HCl) through the period of 21 days. The pH was kept constant at 0.5 and the bath was kept at room temperature (i.e., approximately 20 °C). The volume, weight, amount of the eroded material, and compressive and flexural strength were measured successively after 7, 14, and 21 days of the experiment. Eroded material was stripped mechanically with a spatula and the weight of the samples was measured. The tolerance of the measurement amounted to an accuracy of ± 0.1 g.

Compressive and flexural strength measurements of both sealing mixtures were investigated in the cement laboratory conditions using a laboratory press with a maximum allowable pressure of 300 kN (Fig. 4). Following the API requirement for strength, geothermal wellbore cement has to exhibit a compressive strength of minimum 6.9 MPa after a 12-month downhole exposure to the expected reservoir conditions (API Task Group on Cements for Geothermal Wells, 1985). No requirements for tensile strength exist as from the authors’ knowledge, however, it is recognized that cement tensile strength has a high significance for the wellbore cement design (Kruszewski et al., 2019).

| Curing conditions | Temperature conditions | Pressure conditions | Testing equipment | Representation of borehole conditions |
|-------------------|------------------------|--------------------|-------------------|--------------------------------------|
| Atmospheric       | Ambient                | Ambient            | –                 | The least representative              |
| Thermal           | 80 °C to 220 °C        | Ambient            | Oven              | Representative for the case of severe dehydration |
| Hydrothermal      | 180 °C to 200 °C       | 1.55 MPa           | Reactor           | The most representative               |

**Table 3**

Different curing conditions of both sealant samples imitating downhole conditions applied in this study.

Fig. 2. An oven used to cure Portland and geopolymer sealant samples under temperatures up to 400 °C and ambient pressures (left); A reactor used to cure sealants at hydrothermal conditions of up 200 °C and 1.55 MPa (right).

Fig. 3. A 6 % HCl solution of an “acid bath” test with resting OPC (upper row) and geopolymer (lower row) samples.
Measurements of flowability of a wet OPC and geopolymer blends, to imitate sealant placement in the borehole were carried out in a flow channel by Ratiotex accordingly to the EN 13395−2:2002 standard. A sealant mixture was poured into the locked funnel. After 5, 15, 30, and 60 min respectively, the funnel was unlocked, and the mixture was allowed to flow out into the channel. This procedure was repeated for the mentioned different time intervals, maintaining the same volume of the sealant. The experiment was conducted under atmospheric conditions at room temperature of 20 °C.

The determination of static elastic moduli was carried out in a triaxial press, whereas dynamic elastic moduli tests were carried out using an elastometer (LABEK) under atmospheric conditions of 20 °C and ambient pressures. With this device the resonance frequency between 1 and 150 kHz could be determined. Using the resonance frequency values, the elastic modulus is calculated. An ultrasonic data logger (Vikasonic) was used to record propagation of microcracks during thermal cyclic loading experiments. The samples were submerged in water and the Vikasonic device was used to measure the travel time of the sound travelling through the sample at a frequency of 54 kHz. The permeability of cured sealant samples was established with tests in a pressure chamber. A constant pressure of 4 MPa was established on one side of the sample and the flow rate through the sample was calculated from the volume travelled through the sample in the time of 3 h. To reach a conclusion on the water permeability, Darcy’s law was applied. Based on the API requirements for geothermal wellbore cement, permeability of wellbore annular sealant shall not exceed 0.1 mD during the 12-month downhole exposure to the expected reservoir conditions (API Task Group on Cements for Geothermal Wells, 1985).

4. Results and discussion

4.1. Flowability

The flow behaviour, which represents the success of the placement in the wellbore, of both wet samples is presented in Fig. 5. It can be seen that geopolymers have initially higher flowability than an OPC sample, which later drastically deteriorates. After approximately one hour of the test, geopolymer samples solidify and become practically not workable. The OPC sample, on the other hand, exhibited a rather constant flowability during the test, being workable even after one hour of the measurement.

4.2. Compressive and flexural strength

Curing sealant samples in atmospheric conditions is not a realistic representation of condition in a deep high-temperature borehole. Under such conditions, Portland-based cement, as presented in Fig. 6, exhibits the highest values of compressive and flexural strength after 7 days of the curing, i.e., 40 MPa and 4.2 MPa respectively. The geopolymer blend was not cured under atmospheric conditions as the process of geopolymerization requires elevated temperatures to initiate hardening and solidification. For the case of the oven-cured Portland cement samples exposed to 100 °C and less, where the influence of water evaporation is believed to be negligible, compressive strength falls significantly above the required strength for the annular cement of 6.9 MPa (API Task Group on Cements for Geothermal Wells, 1985). Above the temperature of 120 °C, a clear deterioration in the both compressive and flexural strength of the Portland cement was observed. This is believed to be due to quick water evaporation. The water can no longer be contributed to the setting and hardening process. Another effect of high temperature, which should not be neglected, is the impact on the cured sealant microstructure. Any closed porosity will be destroyed due to increasing pressure inside the yet unstable structure. Continuous porosity will be formed, decreasing not only the strength but also dramatically increase permeability. A substantial rise of the compressive strength between samples with 1 and 7 days of curing process for the Portland sealants was observed. It is also seen, that a flexural strength approaches values that are too low to allow for a reliable measurement (i.e., close to 0 MPa) at curing temperatures above 200 °C. This phenomenon means that rapid failure may occur in the hardened cement in the wellbore (i.e., crack propagation or debonding at cement interfaces) under acting thermo-mechanical stresses. As presented in Fig. 7, which shows the impact of curing conditions and
temperatures on compressive and flexural strength, the strength values of the geopolymer sample are relatively higher than for the case of conventional Portland cement. To obtain the most representative strength values of borehole-like conditions, samples were cured in a reactor under a temperature of approximately 200 °C (180 °C for geopolymer samples) with a vapour pressure of 1.55 MPa. The closed system of the reactor prevents water from evaporation enabling the hardening mixture to acquire higher compressive and flexural strength. A high discrepancy is observed between values of compressive and flexural strength of both sealants, as presented in Figs. 6 and 7, between an oven and reactor-cured samples with the latter ones being significantly higher. It can also be seen that cured in the reactor geopolymer samples show slightly improved compressive and similar flexural strength to the strength acquired by the conventional Portland mixture.

It should be mentioned, that during the laboratory measurements of the cured OPC and geopolymer samples, it takes approximately few minutes to bring the sealant sample from their curing unit (i.e., oven or reactor) to the next measuring device after the initial cooldown of the reactor to the temperature of < 100 °C. In that time, sealant samples will be exposed to the even colder, atmospheric conditions (i.e., approximately 20 °C) and ambient pressures. Such conditions might potentially lead to a thermal shock that could induce surface cracking and influence, later measured, strength and elastic properties. This procedure, however, was the only possible way to manage measurements at such extreme temperature conditions. Sealant samples were always...
transported in a container in bulk to reduce such effects. As measurement of only one sample at a time was possible, the last measured sample was significantly cooler than the first one, resulting in rather high uncertainties in Fig. 6 and Fig. 7, especially for the geopolymer sealants.

4.3. Elastic modulus

Fig. 8 presents results of elastic moduli measurements of OPC and geopolymer sealants cured at different conditions with results of the elastic moduli of geopolymer sealants after five thermal load cycles with a temperature change from 400 °C to 20 °C. Elastic modulus is one of the most important properties of annular cement design in high-temperature wells, as it indicates its resistance towards thermo-mechanical cyclic loading. It can be observed that the elastic moduli of geopolymer systems is predominantly lower than the elastic moduli of the OPC systems. This phenomenon potentially indicates that geopolymers are more ductile and thus more resistant to the thermal cyclic loading. A clear decrease of elastic modulus of geopolymer sealants after 5 thermal cycles was indicated. The exact cause of this change has not been further investigated, leaving unclear if the change can be attributed to harmful causes such as internal cracking and opening of porosities. Elastic moduli of the OPC samples are significantly higher than the ones of geopolymers, exhibiting more brittle behaviour and potentially poor resistance to the thermal cyclic loading. In fact, cracks in the OPC sample were visible by a naked eye after a first thermal cycle (Fig. 9). Therefore, resulting temperature differences that would lead to the cracking of OPC samples might not necessarily lead to the propagation of cracks in the bulk of geopolymer samples. It is observed that OPC exhibits much lower elastic modulus after 7 days of curing at a moderate temperature of 105 °C than samples cured just for a day in temperature of 120 °C for 1 day and then 220 °C for next 6 days.

4.4. Permeability

Results of permeability measurements for OPC and geopolymer blends are presented in Table 4. It is observed that the geopolymer samples exhibit slightly improved permeability, i.e., 0.0122 mD in comparison with 0.0388 mD for the OPC. The resulting permeability of both samples satisfies the required API permeability of 0.1 mD for the annular cement in a geothermal well. However, values presented in Table 4 are representative for sealant samples cured for 7 days at 200 °C and 1.55 MPa. It is expected that the values of permeability for longer cured sealant samples will vary.

Fig. 8. Static (left) and dynamic (right) elastic moduli of the cured OPC (bottom) and geopolymer (top) samples.

Fig. 9. Visible cracks in the OPC sample after one thermal cycle from 400 °C to 20 °C (left) and state of geopolymer samples after eight similar thermal cycles.
4.5. Resistance to the thermal cyclic loading

The samples used in this test were oven-cured at 100 °C for seven days. Prior to thermal cycling, they were cooled down slowly from their oven temperature to the atmospheric temperature of approximately 20 °C over a period of several hours. This long cooling period was intended to minimize the possibility of cracking due to rapid cooling. The samples were then exposed to a thermal cycle. After a first thermal cycle (i.e., the rapid temperature change from 400 °C to 20 °C), the reference OPC mixture showed significant damage, which was visible with a naked eye after sample investigation as presented in Fig. 9. After three such cycles, all of the OPC specimens were severely damaged to the point that the strength test was no longer feasible. Strength measurement of the geopolymer blend, cured under the same conditions, after thermal cyclic load tests, i.e., four thermal cycles with temperature change from 400 °C to 20 °C, resulted in compressive strength in the ultrasonic data logger, was observed. However, the compressive strength is slightly below the values reported earlier for the geopolymer mixture.

4.6. Influence of fibres

None of the introduced fibre types turned out to be suitable as potential additives to the here presented sealing systems for a high-temperature geothermal well application. Pretesting indicated that stainless-steel and steel fibres would lead to segregation and unwanted fibre distribution. High densities in the order of ~7900 kg/m$^3$ of the stainless-steel led to the accumulation of the fibres on the bottom of the container during mixing and on the bottom of the sealant samples after pouring the sample into the moulds. As the described mixing routine might differ to mixing conditions in the field, investigation with a different applied mixing standard may clarify this finding. Direct contact of the sealant with the hostile reservoir fluids of low pH, over the lifetime of a well, might lead to the dissolution of the fibre material. This is especially the case for steel- and glass fibres. Steel and glass fibre might not be stable over the full pH-range. The polymer fibres, on the other hand, began to melt at temperatures below 100 °C, which is considered insufficient for this study. The polymer fibres became more malleable at temperatures above 100 °C which decreased their tensile strength rapidly. This might also induce volume changes that could lead to embrittlement of the whole structure. Once temperatures were further elevated to 200 °C, it was indicated that polymer fibres began to melt within the sample which resulted in low and unmeasurable flexural strength values. Alkali resistant glass fibres seem to be the most promising candidates. The main problem with alkali-resistant glass fibres is connected to the huge fluctuations of the elastic modulus which alters the effective tensile strength. The fibre which was considered and available has a given elastic modulus between 40 and 90 kN/mm$^2$ (Harex, 2019). This significant variation does not provide reliable quality. However, considering the application of the sealant in the deep wellbore, even after finding a good match for the fibre the distribution of fibres inside the sealing system is a significant challenge. In such applications, proper directional flow control is needed. The selection of appropriate fibres is therefore not easy and dependent on the individual mixture and circumstances.

4.7. Acid resistance

During an acid resistance measurement, a clear reaction of the “acid bath” on the OPC samples, by the formation of a white layer, was visible within a relatively short duration of the test. Mechanical stripping with a spatula led to the detachment of this layer from a Portland-based cement sample, as presented in Fig. 10. Below the eroded layer, another dark yellow-brownish one was observed. The geopolymer samples, on the other hand, showed no visual abnormalities and remained untouched by the acid solution.

The weight of geopolymers increased by a few percent during an acid resistance test. The samples were weighed after brief drying with paper cloth. As no colour and geometry changes were observed it was concluded that the weight increase can be attributed to a small amount of an acid fluid filling the pore space in the sample’s matrix. The weight of the reference OPC mixture, on the other hand, decreased substantially. Portland-based cement samples lost about 6 % of their weight after two days during an “acid bath” without any mechanical stripping. Once the eroded outer layer was removed by a light mechanical treatment with a spatula, the weight loss, which might be potentially caused by washing out and erosion resulting from the powerful production fluid flow from a deep high-temperature well, was significantly increased. In the case of geopolymer samples, no removal of the surface, even by vigorous mechanical stripping, was possible. Thus, the weight loss of geopolymer samples in the “acid bath” can be regarded as negligible. In Fig. 11 each point represents the average weight values of tested samples after mechanical stripping of the eroded layer compared to the initial weight before mechanical stripping. It was observed that after 21 days of the test, only 61 % of the OPC sample weight and 58 % of its volume was retained.

Additionally, compressive and flexural strength tests of samples exposed to an “acid bath” were investigated and presented in Fig. 12. In the first seven days (not shown in Fig. 12) the compressive strength of the reference OPC mixture substantially increased. In the case of geopolymer samples, the compressive strength decreases quite sharply within the first 7 days of the test. From the 7th day onwards, geopolymer sealants showed an upward trend, whereas the reference Portland-based cement mixture a downward trend, of the compressive strength. Despite an increasing compressive strength, a strong downward trend in the flexural strength of geopolymers was observed, similarly to the OPC samples, however with significantly lower strength.

### Table 4

| Parameter                     | OPC     | Geopolymers |
|-------------------------------|---------|-------------|
| Initial volume of fluid, ml   | 171     | 136         |
| Resultant volume of fluid, ml | 166     | 135         |
| Duration, min                 | 152     | 172         |
| Sample diameter, cm           | 1       | 1           |
| Sample length, cm             | 2.5     | 2.5         |
| Viscosity of working fluid, cP| 1.0087  | 1.0087      |
| Inlet pressure, MPa           | 4       | 4           |
| Outlet pressure, MPa          | 0.1     | 0.1         |
| Permeability, mD              | 0.0388  | 0.0122      |

### Fig. 10

Results after 7 days of an “acid bath” in a 6 % HCl solution (upper row – OPC samples, lower row – geopolymer samples).
values. This is believed to be due to the nature of the compressive and flexural strength tests. If the binder between particles decomposes (to a certain degree) compression of the sample will still lead to a measurement of a certain value as the particles are pressed onto each other. For the flexural strength, a portion of particles will experience a tension force. If the binder between particles is decomposed no tensile force can be transmitted and instant failure will be observed. The OPC samples show slightly improved compressive and flexural strength in comparison with the geopolymer samples. This may be potentially due to the water not being able to evaporate from the sample and therefore sufficient amount of fluid was available for the cement hydration processes. It should also be noted that the cross-sectional area of the OPC samples changed a lot and the tested samples were composed of an unaltered core of the heavily attacked samples. It is possible that the low values of flexural strength and relatively moderate values of compressive strength for geopolymer sealant samples might have been connected to the specifics of the measurement. The day which led to the confusion in the obtained laboratory results was after a period when the laboratory was closed for several days and therefore the pH level was not kept constant. This could also lead to the conclusion that the pH value has a significant impact on material properties.
5. Conclusions

Geopolymer sealing systems, investigated in this study, are in no way inferior to the conventional OPC systems as they provide relatively higher compressive and flexural strength than the conventional OPC blends under hydrothermal conditions and at elevated temperatures, better than the OPC mixes resistance to the thermal cyclic loading under the same curing and test conditions, improved ductility, insensitivity towards acids, and lowered CO₂ emission during the manufacturing process. For the future deep drilling projects in high-temperature geothermal fields where direct contact of the casing sealant with highly corrosive fluids is expected, geopolymer sealing systems might be a potentially feasible solution. It is, however, crucial to carry out more extensive laboratory studies, especially including investigations of the shrinkage phenomenon, hardening time, an effect of superplasticizers. Additionally, long-term laboratory tests under high pressures and temperatures in an autoclave system (i.e., reservoir-type conditions), to investigate the long-term performance of non-Portland systems are necessary.

CRediT authorship contribution statement

Michał Kruszewski: Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Visualization, Investigation. Marvin Glissner: Formal analysis, Investigation, Resources, Data curation, Writing - review & editing, Validation. Simon Hahn: Supervision, Writing - review & editing. Volker Wittig: Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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