Impact of Drilling Fluid Contamination on Performance of Rock-Based Geopolymers

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Summary
Our objective is to present selected rheological and mechanical properties of rock-based geopolymers contaminated with different concentrations of drilling fluids. The possible flash setting and the maximum intake of drilling fluids before seeing a dramatic deterioration of the geopolymers are presented.

Rock-based geopolymers designed for cementing conductor and surface casing were prepared and cured for up to 28 days at 22°C and atmospheric pressure. Water-based drilling fluids (WBDFs) and oil-based drilling fluids (OBDFs) were designed in accordance with the recommendations from the petroleum industry. The fluid samples were prepared, and their viscous behavior was characterized before and after hot-rolling. The geopolymeric slurries were mixed and then blended with the prepared drilling fluid volumes. The contaminated geopolymeric slurries were cured and tested at different time intervals. American Petroleum Institute (API) Class G neat cement was used as a reference. These samples were cured and contaminated with the same drilling fluids. The properties of contaminated geopolymer slurries were benchmarked with those of the contaminated Class G cement.

The obtained mechanical properties showed that the rock-based geopolymers are more sensitive to WBDFs than to OBDFs. However, for contaminated Portland cement samples, the obtained results were opposite, and the contamination effect of OBDF on cement was more noticeable than WBDF. The impact of geopolymer contamination is a function of curing time. Although geopolymeric samples showed dramatic strength retrogression at the early time, strength buildup of the samples compensated for the impact of contamination.

Introduction
Well integrity is the central goal for every exploration and production company to ensure safety for humans and the environment. Cement is used to seal the annular space between casing and formation to prevent the undesired flows of hydrocarbon fluid, protect the casing from the corrosive fluids, and anchor the casing in place (Nelson and Guillot 2006). The cement sheath experiences many challenges while coming into place and after placement. These may refer to contamination with drilling fluids, gas attack while setting, geotechnical stresses, thermal loads, and operational stresses (Brandl et al. 2011; Adjei et al. 2020; Wu et al. 2021). The integrity of cement is challenged over time as the well is put on production, resulting in hydrocarbon flowing through the annulus and creating health, safety, and environmental issues.

Contamination of cement with drilling fluid during cementing operations is among the challenges that affect the cement performance and might appear in microannulus form and could go up to the entire cement sheath, or deteriorate the mechanical properties of cement. Different mechanical and chemical aids, such as wipers, spacers, and chemical washes, are used to minimize cement contamination risk. However, some traces of drilling mud will stay in the annulus. As a result, the cement will be contaminated with drilling fluid, which leads to degradation of the cement integrity (Arbad and Teodoriu 2020).

Generally speaking, good cement bonding or shear bonding means contamination-free cement. However, independent of the selection of cementitious material, contamination might also be a necessity for obtaining bonding to the casing and formation. Because of the no-slip condition during displacement, complete displacement may not be possible as a result of hydrodynamic forces alone. An intermixing of fluids including filter cakes is necessary to obtain bonding. Hence, the cementitious material sheath close to any solid boundary is vulnerable for contamination, and these are the positions where deteriorated properties have the largest consequences.

Several studies have been conducted on the cement contaminated with drilling mud to investigate the effect of contamination on the mechanical properties of ordinary Portland cement (OPC). Aughenbaugh et al. (2014) revealed that cement’s compressive strength could be reduced up to 60% from its initial strength when the percentage of contamination with water-based mud is approximately 15% by volume. The thickening time may be reduced, which leads to the setting of cement at unpredicted depth and causes well integrity issues. Abdel-Alim and El-Sayed (1995) showed that OPC lost approximately 80% of its strength when it is contaminated with a high concentration of drilling fluid. They used three types of drilling fluid (i.e., oil-based, water-based, and partially hydrolyzed polyacrylamide polymer mud) with different percentages of drilling fluid (10, 20, 30, 40, and 50%) by volume of cement. His study showed that each type of drilling fluid has a different effect on the properties of cement. Oil-based mud (OBM) has the greatest effect, and contamination higher than 20% should be avoided because it might change the slurry’s flow regime. Cheng et al. (2018) showed that the strength of OPC is reduced by approximately 50% of its original because of the contamination, with 30% of partially hydrolyzed polyacrylamide polymer drilling fluid. Other research, which was conducted on the contamination of cement with OBM, demonstrated that OBM works on decreasing the liquidity of cement and affecting the rheological properties of cement. The porosity and permeability of cement slurry may increase while the compressive strength and bonding strength decrease (Li et al. 2016). Ding (1983) claimed that the cement strength does not depend only on the hydration degree but also on the microstructure of the cement particles. Ding concluded that OBM does not consolidate with cement, and thus, it may create holes in the cement stone. The increase in the percentage of contamination with OBM will result in more holes inside the cement slurry. These holes may destroy the cement structure, which will lead to more reduction in the cement’s compressive strength. Another reason was drawing from the point of the lubrication effect of OBM. Cai et al. (2002) showed that the slippage between the cement particles may happen because of the lubrication effect. Katende et al. (2020) showed that cement degradation increases with the escalations in the dosage of contamination with drilling fluid. Three
experiments have been run with three different dosages of contamination with OBM (5, 10, and 30% by volume). This study demonstrated that the 30% contamination with OBM by volume of cement has the highest degradation among the others. Li et al. (2015) showed that the contamination with OBM decreases cement liquidity. The more OBM added, the more significant the effect on the compressive strength and the cement’s bonding strength. Li et al. (2016) showed that OBM gets dispersed in the cement slurry and forms an oil/water structure. Also, OBM will be bound to the free water of the slurry and form an oil/water/oil structure. These structures will reduce the liquidity of the cement slurry because the free water is tied. Skalle and Sveen (1991) and Aughenbaugh et al. (2014) showed another reason for cement strength degradation. They noted that the phase of high-water activity/low-salinity cement might invert to low-water activity/high salinity because of osmotic forces. The osmotic force would move the free water from the cement slurry to the OBM.

Although Portland cement is the prime material used for zonal isolation and permanent plug and abandonment of wells, because of its limitations, researchers have been looking for alternatives that could replace cement. Of these drawbacks, one may refer to concerns associated with its long-term durability performance, chemical shrinkage, concerns related to contamination with OBM, lack of sufficient ductility, and last but not least, its carbon dioxide emission during manufacturing.

Geopolymers are inorganic materials, formed through geopolymerization of aluminum silicate-based material precursors. Geopolymerization is a process in which aluminosilicate monomers are linked and form a 3D structure made of long molecules. Geopolymers have shown performance in laboratory scale to be used as an alternative barrier material to cement for well cementing applications (Khalifeh et al. 2014, 2016, 2017, 2018; Kajarathan et al. 2015; Salehi et al. 2016; van Oort et al. 2019). Of these geopolymers, one can refer to fly ash-based, metakaolin-based, and rock-based geopolymers. Several studies have been carried out on geopolymers to study their mechanical properties such as compressive strength, tensile strength, ductility, and permeability and shrinkage properties. These results have been benchmarked with oil-well cement. Drawing a straight conclusion on the performance of these geopolymers compared to Portland cement may not be possible because of the inconsistency of the obtained results. This is because of variations in the types of geopolymeric precursors and the design of the alkali silicate solution, and sometimes even because they are not geopolymers but alkali-activated-based cement. Perhaps one of the reasons for not being able to commercialize geopolymers yet for oil-well cementing applications successfully could be the variation in the used geopolymeric precursors and design of the hardener phase. Khalifeh et al. (2014, 2016, 2017, 2018) have been focusing on the development of rock-based geopolymers with less than 10 wt% of calcium content in the mix design. In contrast, the hardener is alkali silicate solution, mainly potassium silicate because of their slurries’ low-viscosity profiles (Khalifeh et al. 2014, 2016, 2017, 2018; Kajarathan et al. 2015; Kimanizi et al. 2020). Their rock-based geopolymeric precursor has been normalized to obtain reproducible results. Pumpability at different downhole temperatures, compressive and indirect tensile strength development, ductility, permeability, chemical shrinkage, long-term durability when exposed to downhole chemicals at elevated pressure and temperature, and heat evolution while setting are among the measured properties of their geopolymers. These data sets make their work unique and make benchmarking with neat G cement an easier task. However, they have not contaminated their rock-based geopolymers with water-based muds and OBMs.

Liu et al. (2017) studied the solidification of alkali-activated Class F fly-ash cement when contaminated with different ratios of nonaqueous drilling fluids. They showed that geopolymers can take up to 30%, by volume, of the drilling fluid. However, they did not reveal the possible mechanism for such behavior. Salehi et al. (2017) conducted a sensitivity analysis on impact of OBM on their alkali-activated fly-ash-based cement. They showed that when their alkali-activated Class F fly-ash-based cement is contaminated with 5% OBM, by volume, the strength of their neat alkali-activated cement was reduced approximately 5%. However, when their samples were contaminated with 10% mud, their sample’s strength reduction was approximately 25%. They did not show the possible degradation mechanism when their samples were contaminated with the OBM. These researchers did not use similar mix designs to study the performance of their samples when contaminated with OBDFs.

The geopolymerization reaction is a complex process in which aluminosilicate species react with hardener (i.e., alkali silicate solution) and hydrogen, oxygen, water, or a combination of them is produced. This process is opposite to the hydration of cement, in which water is consumed by cement. In the geopolymerization process, water is not consumed and remains in the system. Perhaps some of the water can be consumed by calcium content minerals (although there is little calcium content in the precursor phase), and C-S-H (calcium silicate hydrate), or C-A-S-H (calcium aluminum silicate hydrate) gels are formed. Water helps ions to be transported through the system.

In the following, the impacts of WBDFs and OBDFs on the mechanical properties of the rock-based geopolymer and the contribution of drilling fluid in the chemical reaction during the geopolymerization process are described. Also, neat Class G cement is used in this study to compare its performance and benchmarking with neat G cement. It yielded a slurry density of 1.94 s.g. The mix design of the neat Class G cement and geopolymer is tabulated in Table 2. OBDFs and WBDFs were synthesized in the laboratory according to API standards. Tables 3 and 4 show the mix design of both WBDFs and OBDFs. The density of the WBDFs and OBDFs were measured as 1.31 and 1.2 s.g., respectively.

### Experimental Procedures

**Materials.** The compositions of rock-based geopolymers are shown in Table 1. The geopolymeric slurry was prepared by mixing potassium silicate solution (sodium sesquioxide/potassium oxide ratio of 3:1) with the precursors. The hardener-to-precursor ratio was selected to be 0.524, which yielded a slurry density of 1.97 s.g. For comparison, a Portland cement slurry was prepared of a Class G cement and 44% by weight of cement (bwoc) water according to API standards. It yielded a slurry density of 1.94 s.g. The mix design of the neat Class G cement and geopolymer is tabulated in Table 2. OBDFs and WBDFs were synthesized in the laboratory according to API standards. Tables 3 and 4 show the mix design of both WBDFs and OBDFs. The density of the WBDFs and OBDFs were measured as 1.31 and 1.2 s.g., respectively.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>CaO</th>
<th>MgO</th>
<th>Na2O</th>
<th>K2O</th>
<th>TiO2</th>
<th>MnO</th>
<th>SrO</th>
<th>BaO</th>
<th>S2-</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>60.43</td>
<td>10.56</td>
<td>0.57</td>
<td>15.03</td>
<td>8.08</td>
<td>1.76</td>
<td>1.55</td>
<td>1.15</td>
<td>0.0097</td>
<td>0.0097</td>
<td>0.005</td>
<td>0.61</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 1 — Chemical composition of the geopolymeric precursors.

<table>
<thead>
<tr>
<th>Type of Slurry</th>
<th>Solid (g)</th>
<th>Liquid (g)</th>
<th>Density (s.g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat API Class G cement</td>
<td>792</td>
<td>348</td>
<td>1.94</td>
</tr>
<tr>
<td>Neat geopolymer</td>
<td>700</td>
<td>367</td>
<td>1.97</td>
</tr>
</tbody>
</table>

Table 2 — Mix design of the slurries.
Test Procedures. The slurries of both rock-based geopolymers and Class G cement were prepared according to API RP 10B-2 (2013). Different dosages of drilling fluids were introduced to the rock-based geopolymer for 10 seconds. The contamination intensity of rock-based geopolymer was decided to be 5, 10, 15, and 20 wt% (by weight of precursors). Afterward, the geopolymer pastes were poured into plastic molds for curing on different days. The molds are cylindrical plastic molds 100 mm in length and 52 mm in diameter. The samples were cured for short-term (1, 3, 5, 7, 14, and 28 days) and long-term studies (3, 6, and 12 months). The same procedures were followed for the Class G cement slurry. Neat recipes of the geopolymer and cement were used to compare and clear the impact of contamination on the mechanical properties of the materials.

The compressive strengths of the hardened slurries (geopolymer and cement) were obtained by crushing the cured samples. All compressive strength values reported here were based on an average of three molds. The error bars in the figures refer to the standard deviation. A Young's modulus was calculated based on the elastic region of the uniaxial compressive strength plot. The loading rate used for crushing samples was 36 KN.

A commercial viscometer was used to measure the rheology properties of the material following API standards. The effect of the contamination with drilling fluids on viscosity of the geopolymeric slurries was also investigated by means of the viscometer.

Results and Discussions
Mechanical Strength. The results of compressive strength for neat samples of geopolymer and G cement are illustrated in Fig. 1. It is revealed that cement has a higher early development strength than the geopolymer. The cement strength reached a plateau after 14 days and continued with the same value up to 28 days (40 MPa). However, geopolymer kept on developing its strength over time.

![Fig. 1—Uniaxial compressive strength of neat geopolymer and API Class G cement.](image-url)
Fig. 2 shows the impact of contaminations with OBDF and WBDF on the compressive strength of the geopolymer. The contamination with different dosages (5 to 20%) of OBDF reduced the strength of geopolymer paste. Increasing the proportion of contamination from 15 to 20% hardly reduced the compressive strength. Fig. 3 shows the effect of 5% contamination with WBDF on the geopolymer strength. All contaminated and uncontaminated samples build their strength over time.

Fig. 2—Impact of drilling fluid contamination on the geopolymer. (Left) Geopolymer contaminated with OBDF. (Right) Geopolymer contaminated with WBDF.

Fig. 3—Impact of drilling fluid contamination on neat G cement. (Left) Neat G cement contaminated with OBDF. (Right) Neat G cement contaminated with WBDF.

The geopolymer material cannot build any strength when the percentage of contamination with WBDF exceeds 5%. 10% (by weight of precursors) WBDF is mixed with geopolymer and left up to 3 months. This sample had just a gelation form and did not build any strength. Geopolymer reaction is not a hydration process but geopolymerization. Geopolymerization reaction may yield water, oxygen, or hydrogen, depending on the reaction and the curing condition’s kinetics. This means water will not be consumed but produced. Therefore, the introduction of any additional water to the mixture can endanger mechanical properties and long-term durability of geopolymers.

Fig. 3 shows the effect of contamination with drilling fluid (oil and water) on Class G cement’s mechanical properties. It is noticed from both figures that all samples develop their strength over time. The growth in the percentage of contaminations will result in more decline of the compressive strength. The reduction in compressive strength caused by the contamination with OBDF is more than with WBDF.

Reduction in Young’s modulus means more flexibility of material, but cementitious materials are known to develop strength over time. In other words, there are two counteracting parameters to consider when deciding on the material to use as a barrier candidate. Therefore, it is necessary to consider compressive strength divided by Young’s modulus to evaluate flexibility. Analysis of compressive strength to Young’s modulus data shows that the cured geopolymer with or without contamination is more flexible than neat and contaminated Class G cement. In Figs. 4 through 6, a comparison between cement and the geopolymer is shown. Also, it is shown in these figures that the flexibility of the geopolymer decreases over time; however, the geopolymer still has more flexibility than Class G cement. Although the contamination with OBDF increases the flexibility of cement slightly, flexibility of the geopolymers increased noticeably for samples cured up to 28 days at room temperature.

Contamination with 5 wt% of WBDF shows that the geopolymers have higher initial compressive strength to Young’s modulus ratio compared to the API Class G cement data (Fig. 7). However, over time, structure development of the geopolymers results in stiffer material, and the compressive strength to Young’s modulus ratios approach each other.
Rheology Test. All the samples showed non-Newtonian shear thinning behavior as their viscosity decreased with an escalation in shear rate. The neat geopolymeric slurry showed a higher-viscosity profile compared to the neat API Class G cement slurry (Fig. 8). It is mainly due to the length of oligomers formed during conditioning of the slurry. Fig. 9 clarifies the outcome of the contamination with drilling fluids on the viscosity of the geopolymer. Contamination of the geopolymer with WBDFs and OBDFs resulted in lower
shear stress at higher shear rates. In other words, drilling fluid contamination showed a superplasticizer effect. Liu et al. (2019) studied the impact of drilling fluid contamination on alkali-activated fly ash, and they observed a reduced viscosity profile of the contaminated samples. On the other hand, the contamination with OBDF led to an increased viscosity of cement (Fig. 10). However, the contamination of Class G cement with WBDF reduced the slurry’s viscosity (Fig. 10).

Fig. 7—Compressive strength to Young’s modulus ratio of geopolymer and Class G cement contaminated with 5-wt% WBDF.

Fig. 8—Rheology comparison of neat geopolymer and neat Class G cement.

Fig. 9—Impact of drilling fluid contamination on rheological behavior of the geopolymer. (Left) Geopolymer contaminated with WBDF. (Right) Geopolymer contaminated with OBDF.
Conclusions

Performance of the geopolymer (rock-based geopolymers) and neat Class G cement contaminated with WBDFs and OBDFs were studied. The barrier materials were designed for low-temperature applications. The neat Class G cement contaminated with OBDF shows an increased rheology profile while reducing the rheology profile when contaminated with WBDF. Geopolymer contaminated with both drilling fluid systems shows a reduced rheology profile. Considering 28-day curing of samples at ambient conditions, the neat Class G cement reached plateau compressive strength, whereas the neat geopolymer shows continuous strength development.

Contamination with WBDF. The geopolymer is more sensitive to contamination with WBDFs than the neat G cement. Exceeding 5 wt% of WBDF contamination will cancel the geopolymerization process, and material can only develop gel structure. The neat G cement can tolerate contaminations of approximately 20 wt%, although its mechanical properties are affected. Compressive strength to Young’s modulus ratio of the geopolymer shows a higher value than the Class G cement data. It is an indication of a more flexible material while developing mechanical strength.

Contamination with OBDF. Class G cement contaminated with OBDF shows the contamination response and leads to lower strength development. However, the geopolymer creates dispersed oil in the slurry and shows lower strength reduction. When considering curing at room temperature up to 28 days, contamination with drilling fluid will reduce strength development and make the materials more flexible. However, the geopolymer shows much higher compressive strength to Young’s modulus ratio than the Class G cement contaminated with OBDF.

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References
