Evaluation of Qusaiba Kaolinitic Shale as a Supplementary Cementitious Material in Lightweight Oil-Well Cement Formulation

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ABSTRACT: Metakaolin is a supplementary cementitious material produced through the calcination of kaolinitic rocks. The scarcity of high-grade and commercial quantities of kaolinitic-based rocks makes metakaolin expensive. The objective of this study is to evaluate the feasibility of the kaolinitic shale obtained from the mud-rich Qusaiba Member of Saudi Arabia as a source of metakaolin. The rock was dried, ground, and passed through a 75 μm sieve to obtain a fine powder. The powder was calcined at 1202, 1292, 1382, 1472, and 1562 °F for 1 h. The optimum calcination temperature required to convert the material into metakaolin was found to be 1562 °F using X-ray diffraction, Fourier transform infrared spectroscopy, and thermogravimetry analysis techniques. The analytical techniques indicated that the kaolinitic shale is of high grade and less ordered, which would make it an excellent source of a highly reactive metakaolin. Cement systems designed at 12.5 ppg (1.50 g/cm³) with the metakaolin produced from the Qusaiba kaolinitic shale as 30% cement replacement exhibits mechanical properties that would be ideal for downhole oil-wellbore applications.

1. INTRODUCTION

Supplementary cementitious materials (SCMs), also known as pozzolans, are materials that contain amorphous compounds and have the pozzolanic property which allows for interaction with the calcium hydroxide produced when the cement hydrates in water, producing extra calcium silicate hydrate (C–S–H) that improves the strength and durability of cement composites. Examples include fly ash, silica fume, slag, metakaolin, calcined bentonite, rice husk ash, and perlite. The demand for materials with pozzolanic property increased because of the need to reduce the reliance on Portland cement whose production discharges enormous quantities of CO₂ into the atmosphere. Clay, a naturally occurring pozzolan, becomes more reactive when heated. Kaolin is a clay composed primarily of a hydrous aluminum silicate mineral known as kaolinite [Al₂Si₂O₅(OH)₄] and, in some cases, proportions of minerals like montmorillonite, anatase, illite, iron oxides, quartz, feldspar, and pyrite. When the clay is heated within a certain temperature range for a specific period, the present clay minerals undergo dehydroxylation (removal of bound hydroxyl ions), lose their crystalline structure, and transform into a highly reactive SCM known as metakaolin (Al₂Si₂O₅). The degree of pozzolanicity of metakaolin is controlled by many factors. For instance, the optimal calcination temperature is dependent on the source of the rock as the dehydroxylation temperature is affected by the crystallinity of the kaolinite. Badogiannis et al. reported that cement systems made with Greek Kaolin heated at 1202 °F for 3 h showed superb characteristics. Moodi et al. studied different Iranian kaolin and observed that an optimal degree of dehydroxylation was achieved at heating temperatures of 1382–1562 °F for an hour. Elimbi et al. evaluated the properties of geopolymer composites designed using kaolin calcined at 842 to 1562 °F and observed that the clay produced the best composites when calcined at 1292 °F. Tironi et al. investigated the effect of heat treatment on well-ordered high-purity kaolin at 1292, 1382, and 1472 °F for 10, 20, and 30 min and observed that the degree of reactivity was affected by both temperature and heating time. Alujas et al. studied the impact of the heating temperatures (932 to 1832 °F) on the properties of kaolin and observed that kaolin calcined at 1472 °F displayed the highest pozzolanic effect, and the compressive strength at 7 days and beyond for cement samples designed with the material was comparable or higher than that of the control sample. Almenares et al. compared the reactivity of kaolin at calcination temperatures of...
1382 and 1562 °F and observed that the kaolin heated at 1562 °F exhibited higher pozzolanicity.

Even though kaolin is scattered across the world, it is often not in commercial quantities, resulting in low production quantities of metakaolin. Additionally, high-grade kaolin which gives highly reactive metakaolin is scarce, contributing to the high cost of metakaolin. Saudi Arabia has huge kaolinitic rock reserves. This study evaluates the characteristics of thermally treated kaolinitic shale, and the properties of lightweight oil-well cement composite developed with the calcined material.

2. MATERIALS AND METHODS

2.1. Materials. 2.1.1. Properties of Cement, Commercial Metakaolin, and Powdered Qusaiba Kalonitic Shale Rock. The Qusaiba kaolinitic shale (QKS) specimen used in this study was collected from the Qusaiba Member outcrops located in the Qassim region, Saudi Arabia. The Qusaiba Member represents thick, Silurian age mud-rich sedimentary units that extend widely within Saudi Arabia. The specimen was crushed down into smaller pieces using a pestle and mortar, oven-dried at 230 °C for 24 h, and then ground into a fine powder (75 μm). The commercial metakaolin (CM) powder was used as received. The Bruker M4 Tornado X-ray fluorescence device was used to determine the oxide composition of the cement, CM, and QKS (Table 1). The locally produced cement is mainly composed of CaO with considerable amounts of SiO2 and Fe2O3. The sum of SiO2, Al2O3, and Fe2O3 of the CM and powdered QKS is greater than 70%, which indicates that the materials are pozzolanic. The QKS has a comparatively significant amount of Fe2O3, which is expected to impact positively on the strength development of cement systems. The mineral phases in the materials, measured with the X-ray diffractogram [Bruker: Cu radiation (λ = 1.54184 Å), scanning angle of 5 to 80° 2θ angle, operating at 30 kV and 10 mA,] are shown in Figure 1. The SEM plus software was used for the phase identification, and the PDF-4+2021 database was used for the mineralogical analysis. The QKS has 77% kaolinite and 22.6% quartz. The cement is composed of tricalcium silicate (C3S) (66.9%), dicalcium silicate (C2S) (26.4), and quartz (6.7%). The CM is composed of approximately 73% quartz, 27% anatase, and a trace amount of halloysite.

2.2. Methods. 2.2.1. Determination of Optimum Calcination Temperature for the QKS. The calcination procedure followed by Almenares et al. was adopted in this work. The powdered QKS was heated in a programmable laboratory oven from room temperature to 1202, 1292, 1382, 1472, and 1562 °F. Then, the temperature was kept constant for an hour, after which the materials were left to cool to ambient room temperature. The characteristics of the raw and calcined QKS were measured using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) (Nicolet 6700, DTGS-KBr detector, 4000–400 cm−1 range), and thermogravimetry analysis (TGA) (SDQT Q600 device by TA Instruments). The samples placed in the TGA were heated at a heating rate of 50 °F/min in an atmosphere of air.

2.2.2. Slurry Design. Approximately 30% of the metakaolin produced from the QKS, referred to as-produced metakaolin (PM) and calcined at the optimal temperature, and the CM were used in the design of approximately 12.5 ppg (1.50 g/cm³) lightweight systems. It has been reported that metakaolin exhibits enhanced properties when used at 30% ordinary Portland cement replacement. The mix design is given in Table 2. The amount of each component was computed based on mass balance calculations. Generally, sodium bentonite is used in lightweight systems to eliminate free water and improve the stability of the systems. The sodium bentonite was presheared at 12 000 rpm for 5 min. The difference in the water/cement ratio required to achieve the desired slurry density is due to the difference in the specific gravities of the CM and PM. The cement systems developed using the CM and PM were tagged CM_S and PM_S, respectively. The rheological properties, thickening time, and mechanical properties of these systems were investigated. The mixing and testing procedure was according to that recommended by API RP 10B and API SPEC 10A. The OFITE 900 viscometer was used to perform the rheology test at 114 °F and atmospheric pressure. The thickening time was performed at 114 °F and atmospheric pressure with a Grace atmospheric consistometer to determine how long the slurry would remain pumpable.

2.2.3. Mechanical Properties. The crush strength, scratch strength, and elastic constants (Young’s modulus and Poisson ratio) were used to analyze the mechanical properties of the cured specimen. The Tinius Olsen hydraulic press (loading rate of 100 mm/min) was used to crush cubic cement samples for compressive strength analysis, while the scratch strength and elastic constants of cylindrical cement systems were measured using the scratch test equipment by EPSLOG engineering.

2.2.4. Microstructural Analysis. A JOEL scanning electron microscope (SEM) and the XRD equipment were used to investigate the morphology of the microstructure and pozzolanic reaction, respectively. For the SEM analysis, the fractured specimen was oven-dried and gold-coated, and images of the microstructure were taken in the secondary electron mode. The XRD scan was taken within 5 to 80°, 2θ.

3. RESULTS AND DISCUSSION

3.1. Investigation of Degree of Transformation of QKS. 3.1.1. XRD Analysis. Unlike kaolinite which exhibits a degree of crystallinity, metakaolin has a disordered morphology. The XRD results indicate that the raw kaolinitic shale is mainly composed of kaolinite (77%) and quartz (22.6%). A high proportion of kaolinite in the shale implies that the rock is of high grade and would produce a pozzolan with high reactivity.

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Table 1. Oxide Composition of Cement, Commercial Metakaolin, and QKS

| composition | class | G cement | CM | QKS |
|-------------|-------|----------|----|-----|
| SiO₂        |       | 7.63     | 53.88 | 55.55 |
| Al₂O₃       |       | 1.06     | 43.13 | 27.48 |
| Fe₂O₃       |       | 9.11     | 0.66  | 12.08 |
| CaO         |       | 79.60    | 0.00  | 0.00  |
| SiO₂        |       | 1.32     | 0.00  | 0.00  |
| Na₂O        |       | 0.79     | 0.00  | 0.00  |
| SO₃         |       | 1.32     | 0.00  | 0.00  |
| K₂O         |       | 0.15     | 0.31  | 3.07  |
| TiO₂        |       | 0.00     | 2.02  | 1.49  |
| MgO         |       | 0.00     | 0.00  | 0.33  |
The effect of heat treatment on the powdered kaolinitic rock is compared in Figure 2. It is observed that the major kaolinite peaks at 11.8 and 24.4° 2-θ disappear in all heated samples. However, the kaolinite peak at about 19.4° 2-θ still has a high intensity in the heated samples except for the sample heated at 1562 °F. The disappearance of the peaks associated with the kaolinite mineral is due to dihydroxylation, and it confirms that the kaolinite has been converted into metakaolin.26
ally, no new crystalline phases are observed, indicating that recrystallization did not occur, a phenomenon that characterizes the upper limit of calcination. This investigation suggests that the optimum calcination temperature for the QKS is 1562 °F.

3.1.2. FTIR Analysis. FTIR can be used to obtain details in changes in the structure of the materials due to alterations in their chemical structure. The infrared spectra of the raw and calcined kaolinitic shale are shown in Figure 3. In the previous characterization of the samples, XRD shows kaolinite as the only clay mineral. This would make the FTIR an efficient characterization tool as complications that would arise because of the overlay of characteristic bands are eliminated. In typical kaolinitic rocks, four peaks of kaolinite appear between 3000 and 4000 cm\(^{-1}\), which is the region that corresponds to the stretching of the OH groups. When these four peaks are established, it implies that the kaolinite has a well-ordered structure (Tironi et al., 2012; Bukalo et al., 2017). The presence of kaolinite as the only clay mineral suggests that analysis of the bands in the OH-stretching region is enough to analyze the dehydroxylation process. Based on the obtained results, low intensity and unclearly defined peaks of kaolinite appear at 3685.75 and 3625.33 cm\(^{-1}\) in the raw (unheated) sample, indicating a less ordered structure, which would make the material an excellent source of pozzolan. These two kaolinitic peaks present in the raw sample vanishes and are replaced by a broad band in all the heated samples. Additionally, the intensity of the peaks at 998–1037 cm\(^{-1}\) associated with the asymmetric stretching of the Si–O–Si (Al) band decreases and shifts to higher intensity wavenumber with increasing calcination temperature, indicating a collapse of the microstructure (Tironi et al., 2012; Garcia-Valles et al., 2020). Further analysis shows that the OH-deformation band at 912.51 cm\(^{-1}\) is absent in all heated samples, indicating that dehydroxylation has occurred.

3.1.3. TGA. TGA was used to further characterize the raw and heated QKS. With this method, a small amount of the sample is heated over a temperature range, and the weight loss with temperature is recorded. The plot can be used to infer the presence or absence of components or understand certain
phenomena. Figure 4 compares the weight loss of the raw and heated QKS samples. Weight loss from the initial temperature to 230 °F is attributed to the escape of adsorbed water. Additionally, loss in weight as a result of dehydroxylation occurs within 959 to 1634 °F. All heated samples show slight weight loss; however, the least weight loss occurs in the sample heated at 1526 °F, indicating a higher degree of dehydroxylation.

The above characterization techniques (mainly XRD and TGA) indicate that the optimum calcination temperature for the conversion of the QKS to metakaolin is 1526 °F. Cementitious systems developed with metakaolin calcined at adequate temperature with low recrystallization possess excellent mechanical properties.

3.2. Particle Size Distribution and Specific Surface Area of Cement, CM, and PM. Based on the above studies, the sample heated at 1526 °F was used in the slurry design. The particle size distributions (PSDs) and the specific surface area (SSA) of the PM are compared to the cement and CM in Figure 5 and Table 3, respectively. These parameters do impact the fresh and hardened properties of the cement systems. The data were taken using the Mastersizer 2000 MU laser particle size analyzer. The table shows that the CM has the smallest median size, while the cement has the largest median size. The median size of the PM is intermediate between the two. The significance of the size is reflected in the SSA of the materials, with the sample with the smallest median size having the largest SSA and vice versa.

3.3. Properties of Metakaolin-Based Lightweight Cement Systems. The rheology, thickening time, and uniaxial compressive strength of cement systems designed with the CM (CM_S) and PM (PM_S) were compared. The results are presented in the following section.

3.3.1. Rheology. The rheology of cement slurry is a very important fluid property as it affects the pumping pressure, slurry mixability, friction pressure during placement, and mud displacement efficiency.

Several formulations were investigated during the trial stage to determine the impact of various parameters, for instance, the minimum amount of dispersant required to obtain a mixable slurry. The flow curve and viscosity of the cement systems are shown in Figures 6 and 7, respectively. In comparison to the other rheological models tested, the power law model provided the best fit for the measured rheological data. The model parameters and coefficient of determination ($R^2$) using the power law model are provided in Table 4. All systems have a power law index of less than 1, indicating shear thinning behavior. This is confirmed in Figure 7, where the viscosity reduces with increasing shear rate.

Table 3. Physical Properties of Cement and Metakaolins Used in Cement Systems

| cement systems | local class G cement | CM | PM |
|----------------|----------------------|----|----|
| $D_{10}$ size, μm | 4.92 | 1.43 | 1.64 |
| $D_{50}$ size, μm | 24.34 | 5.37 | 7.96 |
| $D_{90}$ size, μm | 61.40 | 20.07 | 28.87 |
| SSA, cm$^2$/g | 5875 | 16 000 | 13 800 |

Figure 6. Flow curve of cement systems at 114 °F.

Figure 5. PSD of cement, CM, and PM.
mentioned problems, a dispersant instead of water was added. A high dosage of dispersant would affect the stability of the system through the formation of free water and sedimentation. During the trial design, it was observed that a minimum of 4 g of dispersant could improve the mixing and flow properties of the CM system. The designed system was thus tagged CM_S_4, which had a 21.6% reduction in the consistency value. For a comparative study, cement systems were prepared with the PM using 0 g and 4 g of dispersant and were tagged PM_S_0 and PM_S_4, respectively. The PM_S_4 system has the lowest consistency. Very low viscosity may also promote settling and fluid loss.\(^34\) Additionally, it was observed that the presence of such a high amount of dispersant in the PM_S_4 system forced water onto the surface of the slurry, a phenomenon known as bleeding, which would affect the stability and strength of the system.\(^35\)

### 3.3.2. Thickening Time
The thickening time gives an idea of how long the slurry could be pumped before it sets. The time taken for the slurry to attain a Bearden consistency (Bc) unit of 100 Bc is considered the upper limit. However, generally, the target thickening time is often based on the objectives of the operator. Commonly reported consistencies are 40, 50, 60, and 70 Bc.\(^36\)−\(^38\)

As screening criteria, the objective was to select the formulations that achieve 40 Bc in approximately 3 h. The thickening time results are shown in Figure 8. From the figure, the CM_S_0 attains 40 Bc much earlier in about 1 h and 20 min. The CM_S_4 and PM_S_0 show comparative thickening times. However, the PM_S_4 system never showed any sign of thickening even at 3 h and 30 min.

### 3.3.3. Mechanical Properties
The CM_S_4 system shows favorable fluid properties and thickening time. The PM_S_0 system also has better fluid properties and comparable thickening time to the CM_S_4 system. Therefore, the CM_S_4 and PM_S_0 systems were selected as the final recipes, and the mechanical properties of these systems were evaluated after 48 h of curing. Three cubes were crushed for each recipe, and the average was taken as the crush strength. The scratch strength was also evaluated. The compressive strength measured using two techniques is shown in Figure 9.

Both techniques confirm that the 48-h strength of the system developed with the heated QKS (PM_S_0) is higher than that of the system designed with the CM (CM_S_4). The elastic constants [Young’s modulus (YM) and Poisson ratio] of these systems are also presented in Figure 10. For enhanced elasticity or flexibility, a lower YM and higher Poisson ratio are preferred. The YM shows how stiff the system is, and it increases with an increase in compressive strength. From the figure, there is no significant difference between the samples in terms of elasticity.

### 3.3.4. Microstructural Analysis of Hydrated Products
The morphology of the microstructure (Figure 11) of the hydrated cement systems reveals the usual phases: the hexagonal plates of portlandite (P) and the fibrous C–S–H gel. These products occupy the voids, thereby densifying the microstructure. The XRD plot shown in Figure 12 provides a means of analyzing the cement hydration and pozzolanic reaction. Key crystalline phases present in the microstructure include tricalcium silicate, dicalcium silicate, portlandite, anatase, and quartz. The presence of the amorphous C–S–H gel is indicated by the halo hump at 25 to 35°, 2θ.\(^39\) This hump is broader and larger.

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**Figure 7.** Shear rate vs viscosity of cement systems at 114 °F.

**Figure 8.** Investigation of the thickening time of developed cement systems at 114 °F.

**Figure 9.** Compressive strength of metakaolin-based cement systems cured for 48 h at 163 °F.
in the PM_S_0 system in comparison to the CM_S_4 system, qualitatively suggesting the formation of more C\text{−}S\text{−}H gel in the former. Since the C\text{−}S\text{−}H phase is responsible for the strength, the high content in the PM_S_0 system explains its high strength.

4. CONCLUSIONS
This study investigates the feasibility of using the QKS from the mud-rich Qusaiba outcrop in Saudi Arabia as a source of metakaolin.

The following are the salient findings gathered from the study:

1. The XRD and FTIR techniques show that the kaolinitic shale of the Qusaiba formation is less ordered and is composed of a high proportion of kaolinite. These characteristics suggest that the material is of high grade and hence would be an excellent source of metakaolin.
2. The optimum calcination temperature for the kaolinitic shale collected from the Qusaiba formation is 1562 °F.
3. The metakaolin produced from the QKS can be used to develop lightweight cement systems with satisfactory mechanical properties.

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Figure 10. Elastic properties of cement systems cured for 48 h at 163 °F.

Figure 11. Morphology of the hydrated products, left (CM_S_4) and right (PM_S_0), (magnification: ×1000).

Figure 12. Mineralogical composition of the hydrated specimen of CM_S_4 and PM_S_0 systems.
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