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Use of Fly Ash and Metakaolin in Wellbore Cementing to Prevent Alkali-Silica Reactivity of Amorphous Si-rich Components

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ABSTRACT

This study looks at the effects of metakaolin (MK) and fly ash (FA) on alkali-silica reaction (ASR) prevention as well as mechanical and petrophysical properties of light-weight wellbore cement containing silica-based microspheres. The helium gas porosimeter and liquid pulse decay permeameter was used to determine the porosity and permeability of samples respectively. Micro-indentation was used to determine Young's modules and Hardness values, and Scanning Electron Microscopy was used to visualize the microstructural changes. The cement petrophysical properties are enhanced by addition of MK and FA, observed in permeability and porosity reduction, as well as in more dense microstructures. Final conclusions show that both metakaolin and fly ash can prevent reactivity of glass based microspheres in light weight wellbore cement, but metakaolin is more effective in doing so.

1. Introduction

Cementing is a required process for drilling and completing any types of wellbores, those producing geo-fluids, or used for injection of waste fluids. The cementing process is completed by pumping the cement down through a casing string then back up between the formation and casing where the cement forms bonds between the two and seals off fluid flow in this area. These cements used in the wellbore construction are expected to maintain their integrity throughout the life span of the well, often at high temperatures and pressures as well as being exposed to geochemically aggressive fluids. Loss in cement integrity can lead to fluid migration through the cement as well as structural issues that result in costly workovers needing to be completed on the well. Such failures result in HSE accidents that impact society and cause economic loss to the industry. Geothermal wellbores require durable materials, and special cement, such as geopolymers. Aluminate-based cement, have been investigated and redesigned to the same degree as Portland Cement (Pyatina et al. 2016, Pyatina & Sugama, 2017).

In the geothermal reservoirs, the subsurface environment is associated with high T. In order to prevent cement mineralogical changes, known to cause strength retrogression and low structural integrity of cement sheath, various Si-rich materials have been reported as a solution in mitigating strength retrogression. Wellbore integrity issues and potential wellbore cement failure, which becomes an issue if the well cannot maintain its structural integrity as well as the zonal isolation, can potentially allow for uncontrolled and undesired fluid migration. Prevention of this phenomena, which requires the use of silica-rich additives, is normally achieved by the addition of silica flour in regular and heavy weight cement slurry (density above 13ppg). However, for light cement slurries (bellow 13ppg) that can be achieved with glass microspheres, which are not crystalline in nature and are susceptible to Alkali-Silica Reactivity (ASR). Glass fiber can also be a source of ASR, as it can be used to increase fracture toughness of cement (Bellow & Radonjic 2015, Radonjic & Bello 2015).

Lightweight cements can be achieved through a variety of different approaches. The first and easiest is to increase the water ratio of the cement. Although, this method can only be used until the cement slurry reaches a density of 1.55g/cm. after which, the cured cement will no longer be able to provide the necessary integrity of cement. To achieve densities below this value, two main methods can be used. The first method is foaming the cement; where nitrogen gas is mixed into the cement, replacing a portion of the bulk cement, and effectively lowering the density. This method can have instability concerns due to the coalescence of nitrogen forming large channels in the cement allowing for fluid migration ((Pang et al. 2017). The other method is to mix silica-based microspheres into the cement, which have low specific gravities and will lower the density. However, these microspheres have been shown to lead to alkali-silica Reaction (ASR) in the cement. This is due to the high salinity pore fluids reacting with the microspheres forming expansive ASR gel that can lead to loss of structural properties of the cement as it expands as well as cracks(Sabin 2005), (Albers & Radonjic 2017).

ASR has long been studied in cement and concrete research and a variety of methods have been shown to help in the prevention of ASR. These methods typically involve mixing some chemical into the cement that will react with the hydroxides early on so that they are not present in the pore fluid latter to react and break apart the silica content. Different temperatures and silica composition and salinity of the environment are among the conditions that affect ASR (Lingard et al. 2011). Additionally, recent studies have shown confining pressures to control ASR expansion with increasing pressure leading to less expansion (Lingard et al. 2016). Also seen in (Lingard et al. 2016) was that ASR will expand more in the direction of less stress. In the wellbore would mean that more care would need to be taken in understanding how the forces would act on the cement.

Conventionally, this is done by adding pozzolanic materials such as fly ash or slag to prevent ASR (Tang et al. 2015), (Sarfo-Ansah et al. 2014). Additionally, lithium compounds have been shown to achieve ASR prevention as well (Leeman et al. 2014), (Schneider et al. 2010). Metakaolin is another compound that has been shown to effectively work as a pozzolanic material for preventing ASR and leading to higher strength development as well as lower pore space in the cement (Peiliand et al. 2017), (Moser et al. 2010). This study looks at and compares the effects that fly ash (FA) and metakaolin (MK) have on lightweight wellbore cements containing silica-based microspheres as ASR prevention.

2. Methodology

The materials used for this study include Haliburton class H cement, 3M HGS19K46 microspheres with a nominal density of 0.46 g/cc, an average diameter of 20 microns, with survival pressures of up to 19,000 psi. The Fly ash is class F from Halliburton and Metakaolin is from PowerPozz Advanced Cement Technologies.

Research showed that metakaolin works in lower mixed percentages than fly ash. Therefore, this reasoning was implemented to justify the mix percentages of fly ash and metakaolin. The samples were prepared with different percentages (see Table 1), of fly ash and metakaolin to investigate the effects of additives on the cement after one month compared to samples that didn't have preventative additives. Bentonite was also added to prevent solid separation. All samples were made at density of 1.55 g/cm^3 to test a consistent weight that could be used for the same cement slurry design. Mix proportions for both MK and FA, can be seen in Table 1.

Samples were mixed in a Waring laboratory blender in accordance with API 10B recommended practices. Bentonite was pre-hydrated at approximately 16,000 RPM for five minutes, after this time all other solids were mixed in, except the microspheres, at 20,000 RPM for 35 seconds. After this time microspheres were mixed in by hand with a spatula until evenly distributed. After being mixed samples were poured in 7.63x2.54 cm cylindrical brass molds. The samples were kept in the molds for 24hrs at room temperate in order to set and then moved to a closed container containing a solution of calcium hydroxide and deionized water, at pH 13. These containers were placed in the ESPEC environmental chamber at 70^{0}C and 100% relative humidity for 28 days.

After this time, samples were removed from the chamber and prepared for a series of different testing. The first property that was tested was porosity. To do this samples were cut on both ends to a length of 5 cm. The samples were then soaked in acetone for 24 hours to replace the pore fluid and minimized precipitants formed during drying. Next, the samples were left in an oven at 60^{0}C for 24 hours, after which the temperature was increased to 105° C to completely dry sample. After this time porosity was determined using Core Labs UGV-200 UltraGrain Volume helium porosimeter.

Knowing the value of porosity, the value for permeability was determined using the Core Labs Pulse Decay Permeameter for brine/water. In this test, the non-dried cement cores are placed in a rubber sleeve inside a high-pressure container. The container has a pressure of 34.5 MPa, then deionized water is used to move across the core. The entire core system is brought to 2.76 MPa then one end is raised to 3.45 MPa and the pressure difference across the core is recorded with time. Using this pressure change as well as material and fluids properties, a line is created with the slope of the line giving the permeability.

Mechanical properties of the cement were also tested on samples that had not been dried. Micro-hardness was tested using a Nanovea Micro/Nano Module. This device applies a force onto the sample using a micro-hardness Vickers diamond tip and measures displacement of the tip as the load is applied to create a depth-versus-load curve. This curve is then used to calculate hardness and Young's modulus during the unloading portion of the curve.

Table 1: Sample mix proportions, values shown by weight of cement percentages being replaced by supplemental cementitious materials, Metakaolin (MK) and Fly Ash (FA)

Sample	No MK or FA	15% FA	30% FA	8% MK	25% MK
Class H	1	1	1	1	1
Water	0.58	0.66	0.75	0.63	0.75
Bentonite	0.02	0.02	0.02	0.02	0.02
Microspheres	0.08	0.08	0.08	0.08	0.08
Fly Ash (FA)	0.00	0.15	0.30	0.00	0.00
Metakaolin (MK)	0.00	0.00	0.00	0.08	0.25

Finally, to visualize the effects that the different additives had on the cement, Scanning Electron Microscopy (SEM) was conducted. A dual beam-focused ion beam microscopy, FEI Quanta 3D FEG/SEM was used to do imaging in Secondary electron (SEI) and Backscattered Electron (BSE) mode. Samples were dried by the same method as those used for porosity. Then samples were polished down to a 1micron finish, using a series of polishing pads placing the samples in an ultrasonic bath between each pad. After polishing the samples were coated with a conductive carbon coating to prevent charging effects. Imaging was done at 10-20 KV and 27 pA.

3. Results

Table 2 shows the results from the porosity, permeability and indentation tests obtained on cement samples with and without MK and FA. Values shown are averages of 3 samples tested with ± showing standard deviations. In case of porosity and permeability up to 3 measurements were obtained from each sample, and in the case of indentation, 6-12 measurements were obtained per sample in order to reduce the error as a result of cement heterogeneity. Following these trends conclusions can be made about the mechanical and petrophysical properties of these cements.

From the petrophysical point of view, additions of fly ash and metakaolin decreases the porosity of the cement with higher additions of fly ash having a larger impact on porosity as compared to the high additions of metakaolin. These trends with porosity are also counted into permeability with the additives lowering permeability and metakaolin having a larger impact. These results match with those that have been seen in other studies like Shen (Peiliand et al. 2017) and Moser (Moser et al. 2010). Shen showed that at higher levels of metakaolin, ASR effects were less and accompanied by larger reductions in porosity with optimal MK levels being around 10%. Moser showed that metakaolin was more effective at preventing ASR than fly ash because of lower permeability. These decreases in porosities and permeabilities are due to the pozzolanic reactions of curing in the cement. As these reactions occur more, calcium silica hydrate (C-S-H) is formed. This additional C-S-H closes pore spaces inside the cement as well as adding to the cement strength.

Table 2: Porosity, Permeability, Young's Modulus, and Hardness Values of Testing Cement, Average of 3 Samples were tested for porosity and permeability, and each sample was tested 10-12times using micro-indenter, where sample heterogeneity impacts data repeatability significantly.

Property Measured	No MK, FA	15% FA	30% FA	8% MK	25% MK
Porosity (%)	44.81±0.32	29.96±2.05	24.82±1.01	20.79±0.63	19.58±1.04
Permeability (µD)	5.51±0.0	3.96±3.35	1.35±1.25	0.783±0.41	0.503±0.04
Young's Modulus (GPa)	5.68±1.47	5.28±2.22	7.31±1.84	5.15±1.51	4.801±1.68
Hardness (MPa)	56.6±9.67	59.99±20.18	66.2±16.19	57.31±24.93	76.05±13.66

Mechanical property changes are shown to follow different trends than those seen in the petrophysical properties. With hardness at low levels of additions of both fly ash and metakaolin, not much changes when compared to no additions, but at high levels of addition, hardness increases. This trend shows that with higher levels of addition, more pozzolanic materials will create more C-S-H and increase strength. Young's Modulus has a similar trend with low levels of additive not having large changes compared to cement with no additions. But at high levels, fly ash and metakaolin act differently; fly ash increases Young's Modulus while metakaolin decreases the Young's Modulus. Therefore, it can be concluded that metakaolin is making the cement more elastic while fly ash results in more brittle material. This means that metakaolin would be a more desirable material to use in an environment with changing stresses. These changes also mirror the changes seen in previous studies like Shen's (Peiliand et al. 2017) where metakaolin additions resulted in approximately 35% compressive strength addition, which is almost the same value seen in this study.

The image-based investigation was used to visualize the effects these additives had on ASR development. These scanning electron micrographs provide good insight into internal structure and arrangement of various phases present in hydrated cement, with and without MK and FA. Figures 1 to 4 show micrographs at two different magnifications in order to depict a more global view (low mag) and a more detailed view (high mag). Figure 1 shows a microsphere in the cement slurry containing no ASR preventing materials. In this image, the microsphere wall is completely reacted leaving nothing but an ASR and C-S-H gel where the wall once was. In Figure 2 and Figure 3 no reaction is seen with the microsphere wall. These images showing the microspheres not impacted by ASR, and no trace of silica gel, show the prevention mechanisms is effective.

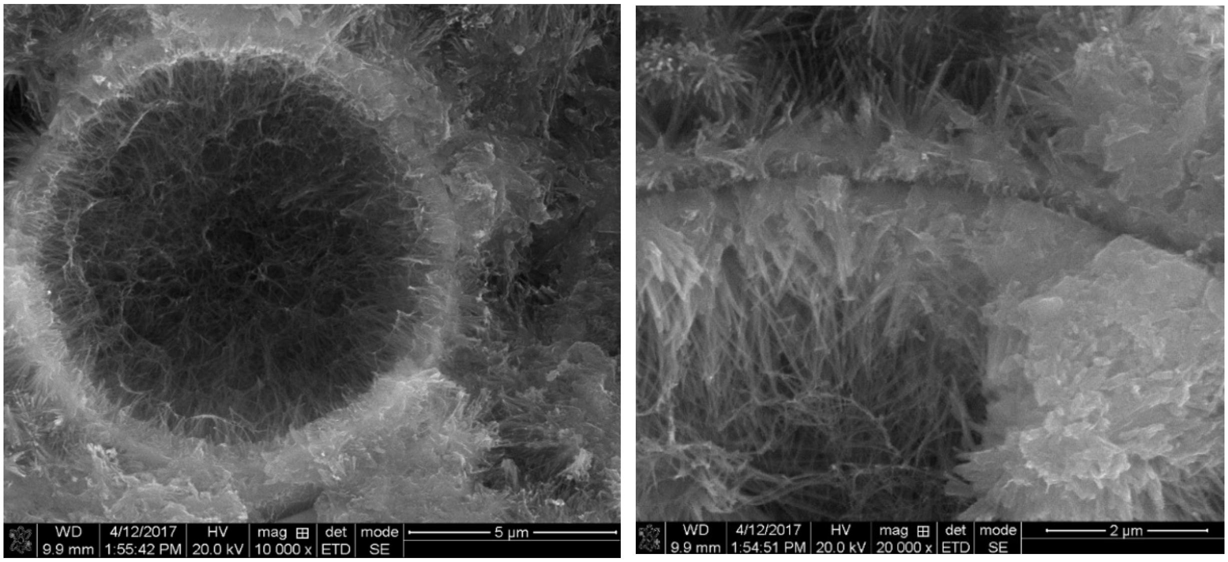

Figure 1: Microspheres from a hydrated wellbore cement sample containing no ASR preventing additives, showing reaction with the cement forming an expansive ASR gel and almost complete transformation of a glass microsphere into ASR reaction product.

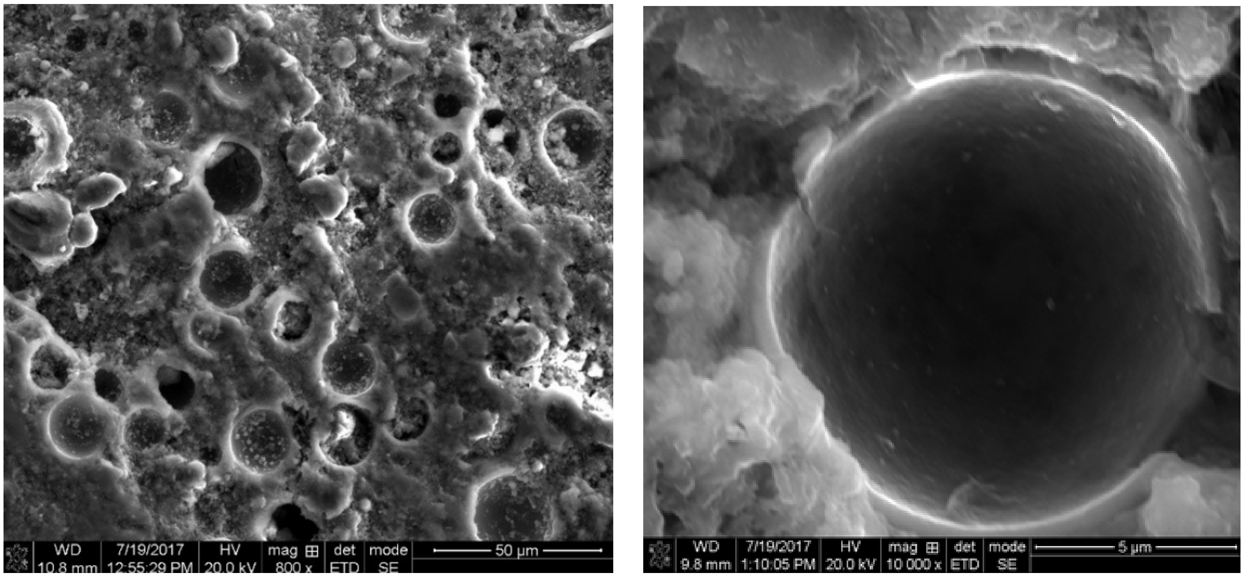

Figure 2: Microspheres from a cement sample containing 25% metakaolin BWC, with walls intact no sign of obvious ASR gel can be seen

These visual observations corroborate with the data from the mechanical and petrophysical properties shown in Table 2. We can report the effectiveness of both, metakaolin and fly ash as ASR preventing additives, in lightweight wellbore cement slurries when glass based microspheres were used and at percentage replacements shown in Table 1. It is important to state that the ASR prevention was not achieved at the expense of petrophysical and mechanical properties, which might be different at different densities of cement slurries and at a different percentage of MK and FA used.

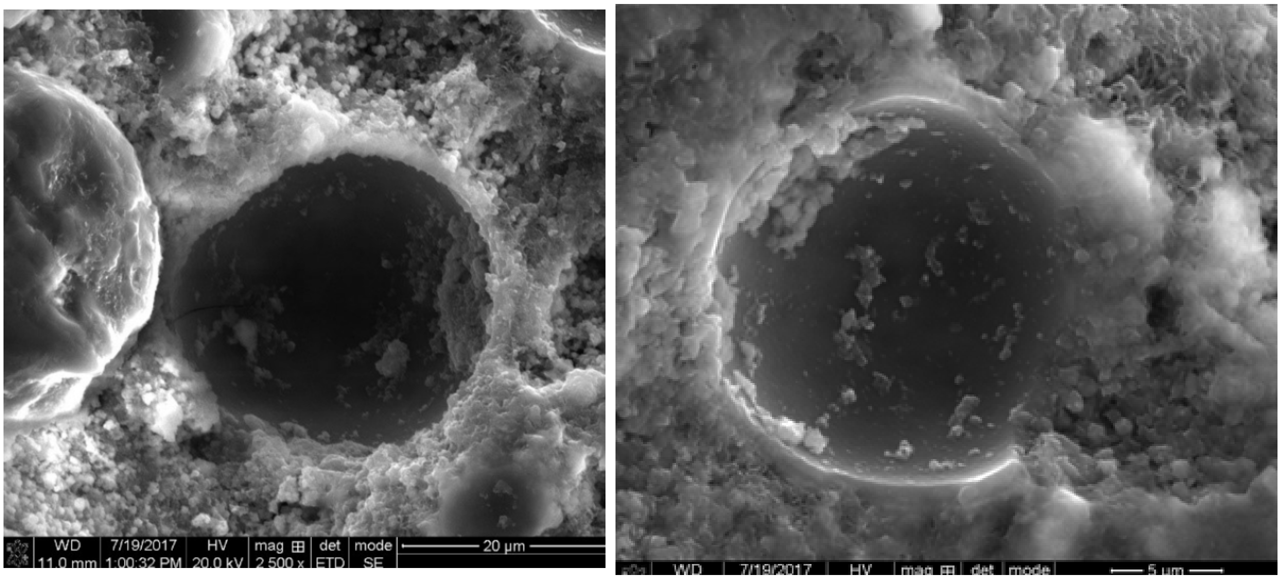

Figure 3: Microspheres from a cement sample containing 30% fly ash with some minor reactions with the cement but nothing appears to be typical ASR gel.

4. Discussion

Wellbore integrity is critical to the lifecycle of every drilled well, and determines if a well is able to stand up to the changing pressures and temperatures as the well is produced throughout the life till it finally gets to the plug and abandonment stage where the well has to be able to stay intact for the rest of time. Having a cement sheath to maintain the structural and petrophysical integrity throughout all of this is essential. For example, in the Gulf of Mexico, where light weight cement is used to complete wellbores in unconsolidated and depleted formations, this is not the case as 43% of 15,500 wells drilled have reported integrity issues (Brufatto et al. 2003). The use of microspheres has the potential to lower the percentage of wellbore integrity issues avoiding use of by not allowing channels of gas to form like with foaming, but ASR must be controlled. ASR can be triggered by different types of amorphous Si-rich materials, but the environment in which the cement is cured has a vast effect on ASR formation.

This study reinforces the effectiveness of using fly ash and metakaolin to prevent ASR and also strengthen cement while lowering permeabilities. This is done through the pozzolanic reactions both of these material lead to the onset of that create additional C-S-H (Snellings et al. 2012). Both are mostly amorphous silica that will react like cement and form C-S-H, but metakaolin is around 40% aluminum oxide whereas fly ash has around 15% aluminum oxide. The SEM micrographs in Figure 4 shows very clearly the negative impact of high alkalinity pore water of Portland cement on the chemical stability of glass microspheres. Even though these types of materials have good testing performance in terms of mechanical stability, where they clearly outperform foam bubbles, their long term stability might cause problems at a later date.

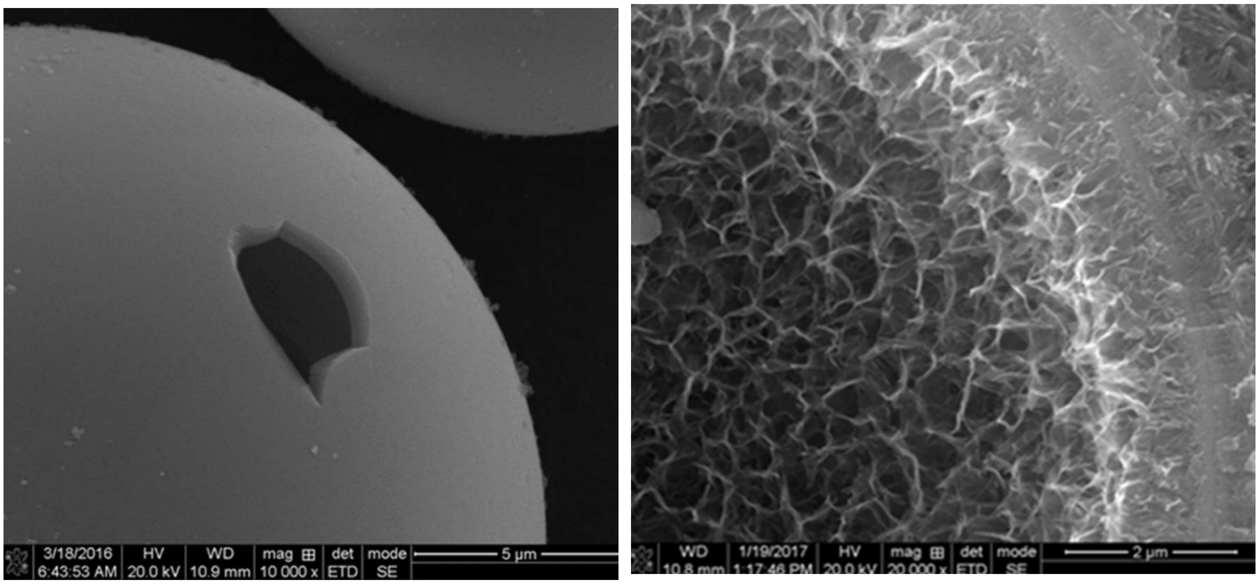

Figure 4: High magnification micrograph of the microsphere surface, as received (on the left), free of any surface deposits and smooth. On the right, a surface of what used to be a glass microsphere, completely reacted, although the spherical shape is still present. This is striking evidence of how detrimental alkaline environment is to glass microsphere's stability and the need for an additive capable of reducing cement slurry alkalinities, such as MK and/or FA or other types of pozzolanic materials.

5. Main Observations and Conclusions

This study showed how metakaolin and fly ash can prevent ASR in lightweight wellbore cements containing silica-based microspheres as well as the impact each had on mechanical and petrophysical properties of the cement. This ASR prevention can be seen visually under the SEM.

Both metakaolin and fly ash lower porosity and permeability with higher mix percentages having larger impacts on both values. Metakaolin addition results to both lower porosities and permeabilities than fly ash with less addition.

Hardness increases with the addition of fly ash and metakaolin; with metakaolin having a larger impact on hardness than fly ash.

Young's modulus was not affected by additions of these supplemental cementitious materials in small percentages, but at high percentages, different effects are seen. Fly ash increases Young's modulus while metakaolin decreases Young's modules.

Because of metakaolin's ability to prevent ASR at lower mix percentages and having a greater effect of mechanical and petrophysical properties, metakaolin is more effective at preventing ASR in lightweight wellbore types of cement containing silica-based microspheres than fly ash.

All of these results also show the importance of testing cement for every job in the conditions that the cement will be used, as everything that changes in the subsurface that might alter the initial cement slurry design, can have long term effects on wellbore integrity over the lifecycle of each well.

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REFERENCES

Pyatina, T., Sugama, T., Moon, J., James, S., Effect of Tartaric Acid on Hydration of a Sodium-Metasilicate-Activated Blend of Calcium Aluminate Cement and Fly Ash, Materials 2016, 9(6), 422; Special Issue Advances in Geopolymers and Alkali-Activated Materials.

Pyatina, T., and Sugama, T., Role of Tartaric Acid in Chemical, Mechanical and Self-Healing Behaviors of a Calcium-Aluminate Cement Blend with Fly Ash F under Steam and Alkali Carbonate Environments at 270 °C, Materials 2017, 10(4), 342; https://doi.org/10.3390/ma10040342

Bello, K., Radonjic, M., Petrophysical and Microstructural Evaluation Of The Thermal Cycle Loading Effect On Geothermal Wellbore, Journal of Porous Media, 18 (2), 137-151, (2015).

Radonjic, M., Bello, K. Experimental Assessment of Cement Integrity under Geopressured Geothermal Reservoir Conditions. Paper presented at World Geothermal Congress, Melbourne, Australia, (April 2015).

Pang, X., Maxson, J. K., Cuello Jimenez, W., Singh, J. P., & Morgan, R. G. (2017, May 1). Microscale Characterization of Field and Laboratory Foamed Cement by Use of X-Ray Microcomputed Tomography. Society of Petroleum Engineers. doi:10.2118/180278-PA.

Sabin, F. (2005). Ultra-Lightweight Cement. CSI technologies. DOE Final Report.

Albers, D. and Radonjic, M. (2017). Prevention of Alkali-Silica Reaction (ASR) in Light-Weight Wellbore Cement Comprising Silicate-based Micro-spheres. Trondheim, Norway. OMAE2017-62015.

Tang, S. Yao, Y. Andrade, C. Li, Z. (2015). Recent Durability Studies on Concrete Structure. Cement and Concrete Research 78: 143-54.

Sarfo-Ansah, J., Atiemo, E. , Boakye, K. , Adjei, D. and Adjaottor, A. (2014) Calcined Clay Pozzolan as an Admixture to Mitigate the Alkali-Silica Reaction in Concrete. Journal of Materials Science and Chemical Engineering, 2, 20-26. doi: 10.4236/msce.2014.25004.

Leemann, A., Lörtscher L., Et al. (2014) Mitigation of ASR by the Use of Li-NO3—Characterization of the Reaction Products. Cement and Concrete Re-search 59: 73-86.

Schneider, J. Hasparyk, N. Silva, D. Monteiro, P. (2010) Effect of Lithium Ni-trate on the Alkali-Silica Reaction Gel. Journal of the American Ceramic Soci-ety 91.10: 3370-374

Peiliang Shen, Linnu Lu, Wei Chen, Fazhou Wang, Shuguang Hu, Efficiency of metakaolin in steam cured high strength concrete, Construction and Building Materials, Volume 152, 2017, Pages 357-366, ISSN 0950-0618, http://dx.doi.org/10.1016/j.conbuildmat.2017.07.006.

Robert D. Moser, Amal R. Jayapalan, Victor Y. Garas, Kimberly E. Kurtis, Assessment of binary and ternary blends of metakaolin and Class C fly ash for alkali-silica reaction mitigation in concrete, Cement and Concrete Research, Volume 40, Issue 12, 2010, Pages 1664-1672, ISSN 0008-8846, http://dx.doi.org/10.1016/j.cemconres.2010.08.006

Brufatto, C., Cochran, J., Power, L.C.D., El-Zeghaty, S.Z.A.A., Fraboulet, B., Griffin, T., Munk, S., Justus, F., Levine, J., Montgomery, C., Murphy, D., Pfeiffer, J., Pornpoch, T., Rishmani, L., 2003. From mud to cement e building gas wells. Schlumb. Oil Field Rev. 15, 62e76.

Lindgard, J. Andic-Cakir, O. Fernandes, I., Thomas, M. (2011). Alkali-silica Reactions (ASR): Literature review on parameters influencing laboratory performance testing. Cement and Concrete Research 42 (2012) 223-243.

Joaquín Liaudat, Ignacio Carol, Carlos M. López, Victor E. Saouma, ASR expansions in concrete under triaxial confinement, Cement and Concrete Composites, Volume 86, 2018, Pages 160-170, ISSN 0958-9465, https://doi.org/10.1016/j.cemconcomp.2017.10.010.

Snellings, R. Mertens, G. Elsen, J. (2012). Supplementary Cementitious Materials. Review in Mineralogy and Geochemistry. Vol. 74 pp. 211-278.