Microporous Spongy Carbon as Compressibility/Elasticity Enhancer

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Abstract

Fluids used in oil exploration/production typically have very low compressibility and are generally considered incompressible. As such, dramatic pressure change can happen in the event of rather small volume change, e.g. pressure drop due to shrinkage or loss of cement slurry during setting or annular pressure buildup (APB). To mitigate the risk to the integrity of a wellbore, it is desirable to use fluid systems that exhibit higher degree of compressibility. In this paper, we explain how compressibility of wellbore fluids can be greatly improved with the addition of an engineered carbon powder.

The carbon powder used in this work has more than 30% by volume of uniform, ultrafine closed porosity within a highly resilient structure. Volumetric change of compressible carbon in liquid was measured by subjecting the test sample to two pressurization and depressurization cycles from 100 psi to 10,000 psi with a syringe pump. In experiments the carbon particulates were found to shrink by about 20% when pressurized to 10,000 psi and rebound back to its original volume when pressure was released. The magnitude of volumetric change was little changed after 10 cycles and independent of the fluid (water, mercury and diesel) used for testing.

This paper will demonstrate the unique properties of this material and explain details of the laboratory testing for a variety of applications in which it was used to reduce amplitude of pressure buildup/pressure drop and increase elasticity/resiliency of cement.

Introduction

During wellbore construction, the annular space between drilled formation and steel casing is cemented over all or part of its depth, to prevent fluid communication between different formation layers. Together with casing, cement serves as an important well barrier and is critical to wellbore integrity. Predominant cause of cementing failure was found to be channels of gelled drilling fluid remaining in the annulus after cement is in place, which can be minimized by adopting cementing best practices for example proper mud conditioning, pipe rotation or reciprocating and good pipe centralization, etc. However, as oil exploration and development activities move into more challenging areas, specialty cement and additives have to be used to meet increasingly more stringent safety and environmental standards, for example in HTHP and Deepwater environment.

Interestingly, some of these challenges encountered are driven by rather small changes in volume of wellbore fluids, for example cement slurry and spacer fluids. As such increasing compressibility of the fluids by adding gas to the liquid phase, i.e. foaming, has proved to be extremely beneficial. One example is gas/liquid migration. As cement starts to set, pressure transition was impaired due to the development of gel structure. As a result, pressure inside the cement column starts to drop due to cement volume shrinkage and fluid loss, as demonstrated in a field study by Cooke C.E. et al. Foamed cement is recognized as a good tool for gas migration prevention. Another example is pressure buildup in trapped annulus, which represents a practical threat to wellbore integrity for offshore wells. Liquid volume expansion upon temperature increase during initial production potentially could lead to catastrophic pressure buildup. One of the best technologies for APB mitigation is to fill the space with compressible spacer fluid. Hundreds of applications have been successfully applied in the Gulf of Mexico.

In the literature, compressible fluids are used exclusively referring to foamed liquids. Besides adding gas, there is yet another, albeit seldom exploited way to increase compressibility of liquid phase, i.e., via addition of compressible solid particles. One possible explanation is the lack of commercially available product which would provide meaningful boost to compressibility. Obviously no solid material is more compressible than the gas phase; on the other hand, especially when made from thermally and chemically stable materials like carbon/graphite, this alternative approach also wouldn't have any stability issues, even under the most extreme downhole pressure and temperature conditions, and hopefully will provide advantages from an economic standpoint, particularly in low-volume applications for example in plug and abandonment (P&A) operation.

Recently a highly compressible carbon product was developed which might be a good candidate for such an application. This compressible carbon is highly resilient and contains large amount of extremely fine closed porosity. Under liquid pressure, its pore volume changes, in a reversible manner, by about 20% for pressure up to 10,000 psi. The energy industry is very familiar with carbon/graphite products as they are widely used as bridging agent to prevent wellbore strengthening) or cure fluid loss. Carbon/graphite products are preferred for the application because of their...
exceptional chemical/thermal stability, minimum impact on rheology, increased lubricity, and better resistance to compressive and shears stress, etc., which are just as valuable for cementing operation.

Zonal isolation has to be achieved during the life of the well and after its abandonment. Even in case cement slurry was placed properly, i.e., good primary cement job, temperature or pressure induced stresses inherent in well operations during the life of an oil/gas well may compromise its structural integrity. Long term wellbore integrity depends on mechanical properties of the cement sheath, such as Young’s modulus, tensile strength, Poisson’s ratio, etc. Flexible particles for example recycled rubber particles and copolymer beads have been applied to improve elasticity of the cement. Petroleum coke and resilient graphitic carbon also showed promise in improving thermal stability and mechanical properties. With much higher compressibility under downhole pressure conditions, compressible carbon may perform even better.

In this paper, properties of this unique carbon product are demonstrated, together with detailed lab testing showing potential benefit in addressing various challenges in oil/gas exploration and development for example annular pressure buildup mitigation, short term gas/fluid migration by reducing pressure drop during cement setting stage, long term zonal isolation by improving elasticity of cement structure.

Results and Discussion

The compressible carbon was manufactured via continuous electro-thermo-purification of calcined petroleum coke in a high temperature fluidized bed furnace. Processing in such a unique environment resulted in a product that has low Helium density but very high resiliency. The latter is defined as percent volumetric rebounding upon pressure release from a compressed state at 10,000 psi. The product contains about 1% sulfur, which was confirmed in chemically stable state, and doesn’t dissolve even when treated with strong acid at 400°F. The material has very low BET surface area and pore volume according to nitrogen gas analysis, which was conducted at ambient or low pressure condition. From nitrogen gas analysis, it is clear that compressible carbon has limited open porosity in its structure. The product also has low impurities and low gas content, as shown in Table 1.

Closed Porosity Determination

Density was measured by Helium pyconometry. It was calculated by dividing sample weight by the volume that can be penetrated by Helium gas at ambient. Low Helium density is good indication of closed porosity. Skeletal density obtained from mercury porosimetry experiment under maximum pressure of around 60,000 psi is recognized as good approximation of true density thus can be used to calculate true volume of solid materials. From the calculation below, closed porosity is about 32% for the grade (6719) with d50 at about 400 micrometers.

\[
\text{Closed Porosity} = \frac{(1 - \frac{\rho_{\text{He}}}{\rho_{\text{Skeletal}}}) \times 100\%}
\]

Where \( \rho_{\text{He}} \) is Helium density obtained from Helium pyconometry experiment, \( \rho_{\text{Skeletal}} \) is skeletal density measured in mercury porosimetry experiment at 60,000 psi.

When product was ground to finer size, some closed pores were exposed. Because of this, Helium density increased with the decrease in particle size. For compressible carbon however it is worth noting that majority (73%) of closed porosity remains even after milling to 15 micron (d50), with Helium density at 1.67 gram/cc. In other words, most of the closed pores are in the micrometer range or even finer.

Compression Behavior in Liquid

From application standpoint, it is interesting to see how those closed pores behave under pressure, particularly when applied through liquid media, for example in water and diesel. A test setup was built for this purpose. Figure 1 showed the schematic of test setup. The Quizix pump (QX-20000, Chandler Engineering) is used to add or retract water or other liquids from the high pressure container, such that system pressure would change according to a preset program. It also serves as measurement device for system pressure and injection volume. A floating piston in the high pressure container divides it into two parts. At the bottom there is only water which serves as conduit of hydraulic pressure, while on top it contains test sample. A small amount of surfactant was added to assist removal of gases from the system. After that, the needle valve is closed and test is initiated with water injection by the syringe pump.

Typically test sample was subjected to two pressurization and depressurization cycles. For better comparison, all curves in Figure 2 were aligned at 10,000 psi by adding a constant. The first intrusion step generally is obscured by open porosity and some level of structural degradation, i.e., closed porosity turned open. Data obtained after the first intrusion/extrusion cycle become a lot more consistent. As shown in the picture difference between data obtained from the second cycle and from the tenth intrusion/extrusion cycle is rather small, and mainly in the low pressure range, possibly due to structural degradation of relatively larger closed pores. For this reason data obtained from the second intrusion/extrusion cycle is used for volume change calculation.

For water, system pressure increased almost linearly with injection volume. To reach a final pressure of 10,000 psi, total water injection was equivalent to 2.9% of total volume. Volume change of carbon can be calculated by

\[
V_{w,c} = V_{p,c} - V_{100,c}
\]

\[
V_{w} = V_{p,w} - V_{100,w}
\]

\[
V_{c} = \frac{m}{\rho_{c}}
\]

\[
Z = \frac{V_{\text{cell}}}{V_{\text{cell}} + V_{\text{dead}}}
\]

\[
\text{Apparent Volume Change} = \frac{V_{c,c} - V_{c,w} \times (1 - Z)}{V_{c}} \times 100\%
\]
Where $V_{p,c}$ is pump volume reading at pressure $p$, with carbon sample addition, $V_{100,c}$ is pump volume reading at the beginning of second intrusion/extrusion cycle, 100 psi, with carbon sample addition, $V_{p,w}$ is pump volume reading at pressure $p$, without carbon sample addition, $V_{100,w}$ is pump volume reading at the beginning of second intrusion/extrusion cycle, 100 psi, without carbon sample addition, $V_{p,c}$ is the volume change observed in experiment at pressure $p$, with carbon sample addition, $V_{p,w}$ is the volume change observed in experiment at pressure $p$, without carbon sample addition, $V_c$ is the volume of carbon sample, $m_c$ is the weight of carbon sample, $f_c$ is Helium density as measured by Helium pycnometry, $G$ is volumetric fraction of carbon in test system.

Based on the calculation, apparent volume change was slightly less than 20% between 100 psi and 10,000 psi, which is more than 5 times higher than water.

Similar experiment was also performed in diesel with the same test setup, as well as mercury through a commercial laboratory following very similar pressure program. Apparent volume change data calculated from those experiments are shown in Figure 3. All curves are realigned at 10,000 psi for better comparison. Slight difference is observed in the low pressure range, which likely is the contribution from small amount of open porosity as also shown in Nitrogen gas analysis. On the other hand, the high pressure data are strikingly similar when tested under those three very different fluids.

Intrusion/extrusion of non-wetting liquid for example mercury at high pressure is routinely used to determine pore/open size information of solid materials, which is calculated according to Washburn’s equation as shown below:

$$P_l - P_c = \frac{4\sigma \cos \theta}{D_p}$$

Where $P_l$ is pressure of liquid, $P_c$ is pressure of gas, $\theta$ is surface tension of liquid, $G$ is contact angle of intrusion liquid, $D_p$ is pore diameter.

Depending on material properties intrusion/extrusion behavior of liquid in open porosity may resemble what was shown in Figure 3; however the fact that similar intrusion/extrusion behavior of compressible carbon was observed in mercury, water and diesel, three liquids that have dramatically different wetting behavior on carbon/graphite surface, proved that is not the case. In addition, Nitrogen gas analysis showed very little pore/open volume in compressible carbon. In other words, majority of the pores are in closed state. If they have failed under extreme pressure and become open, intrusion/extrusion behavior would have been very different during the second cycle, when data was collected for the calculation.

Based on these experimental evidences, it is clear that compressible carbon contains large amount of fine closed porosity. Its volume changes with pressure by about 20% from 100 psi and 10,000 psi, in a reversible manner. When added to water based fluid system, its addition potentially would double or even triple compressibility of the base fluid.

Compressibility data can be extracted from Figure 3. In general compressibility of solid materials is several orders of magnitude lower than what is presented here. As such, compression behavior of closed porosity can be obtained by dividing compressibility data by total porosity. From Figure 4 one can see, even though the material itself is a lot less compressible than gas, at least in the compression step, the closed porosity behaves very much like gas, at 60-70% efficiency when pressure is higher than 5,000 psi. In the low pressure range however, the compressible carbon has much lower compressibility. This behavior is very different from gas whose volume can change dramatically when compressed to thousands of psi from ambient. It is an advantage from an operational standpoint as compressible carbon can be added by simple blending, without needing special equipment.

**Effect on Annular Pressure Buildup (APB) Mitigation**

When fluid is trapped in between rigid structures, steel casing or cement, a small increase in temperature, for example during initial production, would result in huge pressure increase and a practical risk to wellbore integrity. The consequence can be catastrophic for offshore wells as the outer annulus typically is inaccessible. Because of this, APB mitigation is an important part of well planning. One of the most effective technologies that are applied to mitigate the risk is to fill the space with compressible spacer fluids. Nitrogen gas is very compressible. Its addition can substantially reduce magnitude of pressure buildup. However, foam is dynamically unstable. Over time, the gas phase would break out and the fluid loses its ability to compensate for pressure fluctuations. From this standpoint, it might be an advantage to use compressible particles like compressible carbon with porosity trapped within a resilient solid matrix.

A test setup (Figure 5) was built to evaluate performance of compressible carbon for APB mitigation. An assembly similar to what is shown in Figure 1 was used to apply pressure prior to the actual test, to simulate what the material would experience during placement. Typically system pressure would be ramped up to 10,000 psi before dropping back to a desirable level, for example 4,000 psi. The high pressure container was placed in a water bath which is resistively heated. A peristaltic pump was used to circulate water back and forth to ensure uniform temperature in the bath. After stabilizing at a predetermined starting temperature, the needle valve was closed, and water temperature was gradually increased (1°F/min) according to a preset program, with pressure value recorded.

As shown in Figure 6 pressure inside the high pressure container increased very quickly when there was only water inside. Because of limitations of the pressure gauge, experiment was terminated at temperature just above 160°F. Extending the curve to 200°F pressure increase would have been as much as 10,000 psi between 80°F and 200°F. In contrast, system pressure only went up by 4,300 psi in the same temperature range for a mixture containing 20vol% of compressible carbon (6719) in 1.75 ppb xanthan gum fluid.
Adding compressible carbon to cement matrix potentially might help reduce the magnitude of pressure buildup as well. To test this idea, cement composite with 18vol% of compressible carbon addition was made in the lab. After setting at ambient for 30 days, the cement pellets were crushed into pieces that are less than 1 inch in length. Water intrusion/extrusion test was conducted under the same condition as shown in Figure 2. As shown in Figure 7, the volume change behavior was very similar to compressible carbon. Nonetheless the magnitude of volume change was much less because the amount of compressible carbon in the test volume was not as much. After the test, the cement pieces were broken apart and the fractured surface appeared to be wet. With calculation it is clear that all compressible carbon particles contributed to the volume change behavior. The detailed mechanism is not clear. One possibility is that pressure has transmitted through interconnected carbon pieces and porosity within the structure, to the near vicinity under huge pressure gradient like what the cement pieces would experience during testing. However, it is also possible that compression behavior of cement composite has been altered by compressible carbon addition.

This unique compression behavior of cement composite with compressible carbon addition can be very useful in the field. Even when cement is used to cover the full length, poor displacement of drilling fluid may leave gelled mud behind. This phenomenon, together with free fluid on top of cement column which might have separated due to gravity settling effect, have led to multiple casing collapses while drilling geothermal wells in the Molasse Basin in southern Germany. MacEachern D.P. et al. also found it critical to prevent bypassed drilling fluid while cementing tieback casing for a HTHP well located in offshore Gulf of Mexico. Foamed cement was one of the preferred cementing solutions for the application. Because of the low permeability of shale formation, even mild temperature change in the drilling phase potentially can lead to casing collapse in the presence of micro-channels and micro-annuli, due to pressure buildup, as shown by Medina M.G. et al. Adding compressible carbon to the cement slurry at sufficient centration potentially would be a great solution to the problems described above.

**Reduced Pressure Drop during Cement Setting Stage**

Gas/fluid migration is one of the biggest challenges to oil well cementing. Annular gas/fluid flow might be initiated when hydraulic pressure falls below pore pressure of the formation. Evidence of hydraulic pressure declination was shown through field study and also demonstrated in lab setting. Cement volume shrinkage, fluid loss and gel strength buildup are believed to be the main contributors with the first two being the driving force. When gas/fluid migration is a concern, typically cement slurry with low volume shrinkage, low fluid loss and short transition time is used. In addition, cross linkable polymer additive may be blended to make the cement penetrable before sufficient gel strength is achieved. Compressible cement slurry i.e. foamed cement is one of the best ways to deal with short term gas migration problem. According to Rozieres JD et al, the compressed gas would help maintain hydraulic pressure such that the pore pressure within the formation is always overbalanced. Like some carbon/graphite products (e.g. resilient graphitic carbon or RGC), compressible carbon with proper size distribution works great as bridging agent in reducing fluid loss. In addition, in previous experiments we have demonstrated that compressibility of the fluids can be greatly improved with compressible carbon addition, thus potentially mitigating short term gas/fluid migration problem just like foamed cement would do. A lab experiment was designed to demonstrate this effect, specifically in reducing the magnitude of pressure drop during initial setting stage.

The experimental setup was the same as what was used to evaluate performance in annulus pressure buildup mitigation. Fluid containing large amount of barite (50 vol%) was used to simulate cement slurry. The mixture was heated to 200°F and pressurized to a starting pressure of 6,000 psi. The system was then allowed to cool down slowly to simulate cement volume loss. As we can see from Figure 8, in the control experiment, pressure reduced quickly with temperature to zero at 105°F. With 20vol% of compressible carbon addition, the extent of pressure drop was much less, and final pressure was over 3,200 psi after cooling down to 80°F. On reheating the mixture to 200°F, pressure went back up to 6,000 psi. The reduced pressure drop together with less fluid loss potentially makes compressible carbon addition a great solution to short term gas/fluid migration problem.

**Improved Resiliency/Elasticity of Set Cement**
Water intrusion/extrusion test of rubber particles and copolymer beads was conducted using the same device and results are compared with compressible carbon as shown in Figure 9. Platinum cured silicone rubber obtained from ThermoScientific is also included. From the results it is clear copolymer beads and rubber particles are less compressible than water while silicone polymer has the highest compressibility among those grades. Compressibility of platinum cured silicone rubber was about 20% higher than RTV silicone which was tested by Bosma M.G.R. et al.\(^2\). On the other hand, water compressibility was the same which is good confirmation on quality of the test results. Average volumetric modulus of rubber was calculated at 440k psi and copolymer beads at 510k psi, compared with compressible carbon at 52k psi. Clearly, it is a lot more compressible than other flexible particle used in the field.

To investigate whether elasticity of cement would be affected by compressible carbon addition, two sets of cement pellets, with and without compressible carbon addition, were made from type III Portland cement. After curing at ambient for a full month, they were machined into shapes that are 1 inch in diameter and one inch in height. Modulus information was obtained from unconfined compressive strength testing on a MTS Universal Mechanical Tester (Insight 50SL). From Figure 10, it is clear cement with compressive carbon addition is more elastic, i.e., lower modulus. In the meantime, a comprehensive study aimed at mechanical performance for example tensile strength, compressive strength, Young's modulus and Poisson's ratio, following standard oil field test protocol is underway, with the help from a consulting company specializing in oilwell cement.

**Conclusions**

A highly compressible carbon product was manufactured via electro-thermal purification of calcined petroleum coke in a high temperature fluidized bed furnace. At a structural level, it contains more than 30% by volume of uniform, ultrafine closed porosity in a highly resilient carbon matrix. When tested in liquids, its volume shrinks by about 20% upon compression to 10,000 psi, and rebounds back to its original volume when pressure is released. As demonstrated in lab testing, this unique compression behavior could be potentially relevant to the following cementing related applications:

1. Annual pressure buildup mitigation. Experimental evidence showed that pressure buildup can be reduced by more than 50% with 20vol% compressible carbon addition. It works multiple times and is compatible with existing mitigation technologies. Addition to cement solid matrix also helps.
2. Short term gas/liquid migration. Pressure drop can be reduced by more than 50% during cement setting stage due to increased slurry compressibility. As such it could help mitigate short term gas/liquid migration problem and potentially leads to better bonding between cement and casing/formation.
3. Long term gas/liquid migration. Compressible carbon addition could potentially improve mechanical properties of set cement for example lowering the modulus; as a result it would have better chance of maintaining structural integrity under downhole pressure and temperature fluctuations.

**Acknowledgments**

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**References**

**Tables**

Table 1. Properties of Compressible Carbon, 6719

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**Graphics**

Figure 1. Liquid Intrusion/Extrusion Test Assembly.

Figure 2. Intrusion/Extrusion Test of Compressible Carbon in Water.

Figure 3. Compressible Carbon Volume Change with Pressure in Three Different Fluids.

Figure 4. Compressibility of Closed Porosity in Compressible Carbon (6719) Compared with Ideal Gas. Data Calculated from 2nd Intrusion/Compression Step.

Figure 5. Test Setup Built to Evaluate Performance of Compressible Carbon on Annular Pressure Buildup Mitigation.
Figure 6. Performance Evaluation of Compressible Carbon Addition on Annular Pressure Buildup Mitigation

Figure 7. Water Intrusion/Extrusion Test of Cement Composite with and without 18vol% Compressible Carbon Addition

Figure 8. Reduced Pressure Drop of Barite Water Mixture Due to Compressible Carbon Addition

Figure 9. Compression Behavior of Compressible Carbon and Other Flexible Particles. Data Obtained from 2nd Intrusion/Extrusion Cycle

Figure 10. Compressive Strength Testing of Cement Pellets with and without Compressive Carbon Addition