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Degradation of Particulate LCM, the Thermal Influence

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Abstract

Particulate LCMs, such as ground marble, walnut shell, and carbonaceous products, are widely applied in the field to cure fluid loss or prevent loss event from happening, i.e. as wellbore strengthening agents. Degradation behavior has been studied in shear degradation testing or via circulation through a flow loop. As drilling operations expand to more challenging areas and wells get deeper and hotter, temperature effect on degradation behavior warrants further investigation.

In this study, carbonaceous LCMs, walnut shell, and ground marble were tested in a high shear mixer at elevated temperatures or after static aging in a high-pressure cell. Materials were also tested for degradation behavior after subjection to 10,000 psi in a uniaxial hydraulic press.

During hot pressing, walnut shell particles formed a solid pellet after compacting at 10,000 psi when temperature was greater than 200°F. Static aging at 300°F in water for 16hrs resulted in weight loss of 37%. For the same material performance in shear degradation testing decreased with temperature. More fine particulates (-100 mesh) were generated at high temperatures. Significant damage was observed in metallic components (rotor shaft, work heads, etc.) and PTFE bushing.

Impact of temperature on carbonaceous materials was rather limited. Among carbonaceous products, resilient graphitic carbon showed superior performance in resisting structure degradation by both shear and compressive forces.

Ground marble was confirmed to degrade the most under both shear and compressive forces.

Introduction

Particulate LCMs has been successfully in the field to cure loss of expensive drilling fluids and even more importantly, to prevent loss event from happening. Significant savings have been achieved by reducing costly non-productive time (NPT) or via saving of one or more casing points. Generally, for preventive treatment particulate LCMs are blended to the mud and remain circulating in the drilling fluid until the weak formation is drilled through, during which time the particulates may pass through wellbore multiple times. Size reduction has been observed in the field[1], particularly for the coarser fractions. As particle size is critical to the success of wellbore strengthening treatment, materials readily degrade during circulation, ground marble for example, has to be added continuously to maintain proper concentration of larger particulates in the drilling fluid, which can be costly and at times difficult to manage from a logistics standpoint.

Extensive studies have been conducted on degradation behavior of particulate LCM products, both experimentally[2-5] and theoretically[6]. Lab results proved that LCM particulates degrade under high shear conditions, the extent of which differs depending on material type. For particulate LCMs, resilient graphite and nutshell are the best products on resistance to shear degradation. More recently, Grant P. et al studied LCM degradation in a flow loop[3]. Genuine mud pump and turbine was used to drive drilling fluid at rates close to field condition. Resilient graphite was found much better in resisting degradation than ground marble.

In addition, once fluid leaks off in wellbore strengthening applications, particles at fracture opening would potentially be subjected to very high closing force[7]. Preferably, they would maintain their size for optimum strengthening effect. For this reason, better performance in resisting size degradation under compressive stress is also desirable.

Resilient graphite and ground marble are the two most commonly used particulate LCMs for wellbore strengthening purpose, based on literature. Lately, engineered walnut shell product has been applied together with ground marble to provide better resistance to size degradation[8]. As a wood material[9], it is interesting to know how it performs at elevated temperatures, particularly in the presence of many other chemicals for example water, alkali, and other aspects of using this product in the field, for instance how its abrasiveness affect downhole equipment.

Walnut Shell (English walnut) Fine and Medium grades and ground marble samples were obtained from a major service company and screened in house prior to testing. Calcined petroleum coke (CPC) and resilient graphite were crushed in commercial mill to around 400-micron d50 before screening. After appropriate sizing, products were split into multiple identical fractions for further testing. This splitting step was found critical in order to get reproducible results.

Experimental Results and Discussion

Thermogravimetric Study

Thermogravimetric experiment was performed on Netzsch STA 449 F3 Simultaneous Thermal Analyzer in air and argon flow. Gas flow rate was set at 70 ml/min. In all tests, temperature was increased from ambient to 300°C (572°F) at a ramp rate of 1°C/min (1.8°F/min). In Fig. 1, temperature has been converted to Fahrenheit in observance to oilfield terminology.

From DTG curves, it appears that only major event that happened below 300°F was moisture removal. Weight loss was very small, less than 4% in both environments. More complicated reactions that led to major weight changes, in both dry air and Ar, happened at much higher temperatures.

Weight change of ground marble, CPC and resilient graphite was found negligible in the same experiment.

Static Aging in Water

Static aging was conducted in oven at target temperature for 16 hrs. In the experiments, 40.0 grams of 30/40 mesh Walnut Shell particles were placed in 500 ml aging cell and filled with deionized (DI) water up to about 1 inch from top. Product was recovered on 325 mesh screen and dried in oven at 250°F for 16 hrs. Detailed test data is listed in Table 1.

The original Walnut Shell particles lost 5.8% weight while drying in oven at 250°F for 16 hrs. Even higher weight loss was observed after static aging in water and drying at the same temperature. In both cases, weight loss was more than what was predicted by thermogravimetric analysis. It appeared that weight loss continued after it reached the temperature, and water "reacted" with walnut shell particle. Static aging at 300°F resulted in a weight loss of 36.6%. Filtrate was dark brown in color, with only trace amount of solid dust after settling. The filtrate after static aging at 300°F was placed in oven at 200°F until water was removed completely. Resin like substance, about 9% of original weight was recovered, and helium density was tested at 1.44 g/cc. When walnut shell is applied at high concentration in hot wells, due to potential release of large amount of this organic substance, impact on mud rheology may not be trivial. Nanoporosity and surface area increased sharply after static aging at 250°F and 300°F. In essence, the material was partially "activated" at those temperatures. Surface area and porosity were tested on Micromeritics Tristar II Surface Area and Porosity Analyzer without further heat treatment.

Change in size was also observed. As shown in Table 1, drying at 250°F alone generated 8.5% on 50 mesh screen. Combined with significant weight loss, only 53.4% of the original mass was collected above 40 mesh screen after aging at 300°F for 16 hrs and drying at 250°F. As LCM concentration is critical to wellbore strengthening, operator needs to take this into account in the planning stage.

There was no weight change observed in CPC and resilient graphite after static aging up to 300°F.

In this study, walnut shell particles were static aged only in DI water. As walnut shell is clearly very active chemically at elevated temperatures, detailed investigation in real fluids, at the presence of diesel, synthetic and other oilfield chemicals is warranted to gauge its impact on drilling fluid properties before field application.

Shear Degradation Testing

Shear degradation study was conducted on Silverson L5M-A Laboratory Mixer. A generator purpose disintegration head was used in all testing. To test performance at elevated temperatures, the original setup was modified to control fluid temperature, as shown in Fig. 3. This setup can only be used up to water boiling temperature of 212°F, however. Static aging was applied instead for performance evaluation at higher temperatures. After static aging treatment at target temperature for 16 hrs, materials were recovered on 325 mesh screen, dried in air to remove excessive moisture, and then transferred directly to Silverson Mixer without further drying in oven. 40.0 gram of solid samples and 350 ml of fluid were used in each test.

After initial trials with a few walnut shell samples, wear was visible on various components of the mixer. In particular, PTFE bushing became a lot thinner and diameter in the neck area of the rotor was greatly reduced. Noise was generated as rotor was touching the dispersing head, thus both must be replaced. In the manual it stated that all wetted parts were made of 316L stainless steel. After discussion with the manufacturer, a shaft/rotor assembly with hardened journal area on shaft and hardened rotor tips (Silverson part# 7250-SR0017) was purchased and used for further testing. Wear was greatly reduced, however not eliminated after this change. The gap between a new rotor and PTFE bushing was less than 5 milli-inches (125 microns) on each side. In essence, the existence or generation of fine particles (-100 mesh) could be the problem. Once wear begins, it escalates very quickly as more particles can get into the widened gap. In Fig. 2, substantial wear can be seen on both rotor and PTFE bushing after only a few testing with walnut shell samples.

Test in DI water was conducted at 4,000 rpm for only 10 minutes to avoid excessive degradation. After the test, products were recovered on 325 mesh and screened for particle size. Test data is shown in Table. 2. Ground marble degraded the most with only 4.9% remaining on the 40 mesh screen together with 63.6% of fines (-60 mesh). Calcined Petroleum Coke performed better with 28.1% left above 40 mesh. Resilient graphite and walnut shell sample were the two best products in resisting degradation by shear forces. Both has more than 50% left at original size after the test. Walnut shell degraded the least amount when statically aged at 200°F or lower. Above this limit performance dropped rather quickly. Resilient graphite showed no dependence on temperature.

The 30/40 mesh products were also tested in weighted water based mud (WBM), prepared following the formulation published by Scott PD et al[5]. While no significant wear was measured when testing was conducted in DI water in general, experiments in WBM resulted in substantial damage to mixer components. Wear on the work head is particularly pronounced. As shown in Fig. 6, 4 scratching marks are visible on the inner surface. Two were at the very end of the openings of the general purpose disintegrating head, while the other two were on the top and bottom end of the rotor tip. It appeared that some particles got trapped in between fast moving rotor and work head. Gap between rotor and work head is around 15 milli-inches (381 microns), slightly less than 40 mesh (425 microns). Even though there was no measurable change in inside diameter of the work head, product became progressively coarser after shear degradation testing, which made detailed comparison on performance impossible. Effort was made to study wear instead, and, for this reason, mixing was extended to 30 minutes. Weight loss data of the general purpose disintegration head is presented in Fig. 4. Walnut shell caused the most damages, followed by calcined petroleum coke. Wear induced by resilient graphite was the least among the three. As static aging temperature increases, wear on work head reduced, indicating that walnut shell became weaker mechanically.

The original Walnut Shell Medium sample was also tested under the same condition. Surprisingly even more weight loss was measured on the work head. Resilient graphite 400 and 1000 grades, with d50 around 400 and 1000 microns respectively, were tested for comparison and only generated minimum wear on the work head. As 91% of Walnut Shell Medium particles are coarser than 40 mesh, it is assumed that shear degradation behavior won't be affected by the wear on work head. Particle size data after shear degradation testing in DI water and WBM is presented in Fig. 5. For testing conducted in WBM only +100 mesh results were presented as mud solids mostly shown on 200 mesh screen. In-situ heating to 200°F using the modified device as shown in Fig. 3 was applied for comparison. In this particular experiment, fluid was heated to target temperature in 30 minutes before turning on the high shear mixer. After mixing for 30 minutes, fluid was cooled down immediately. The following observations were made:

1. Below 200°F, shear degradation performance of Walnut Shell Medium wasn't affected much by static aging. At higher temperatures, particles degraded significantly more. In other words, they become weaker mechanically.
2. Static aging at elevated temperature promoted fines (-100 mesh) formation during shear degradation testing.

Abrasiveness Testing

Over the course of shear degradation testing, the general-purpose disintegration head lost a few milli-inches in outer diameter. Abrasiveness testing was conducted on Walnut Shell Fine and resilient graphite grades to compare potential damage to metallic surfaces during application. Test procedure was adopted from API Recommended Practice for Laboratory Testing of Drilling Fluids procedure for testing abrasiveness of weighting materials. Zinc coated blades were manufactured by Excel Stamping Co. following specification provided by Fann Instruments Inc. In the experiments, 100.0 grams of solid particles were added to 300.0 ml of 22.5 ppb bentonite suspension, and the blade was rotated at 11,000 rpm for 20 minutes. Wear rate was calculated from weight loss of the blade during testing.

Based on test results in Table 3, walnut shell particles are rather abrasive and have higher tendency to cause damage to metallic surfaces. Resilient graphite on the other hand is not a threat in this regard due to very low abrasiveness.

Performance under Compressive Stress

To compare resistance to size degradation under compressive stress, materials (30/40 mesh) were hydraulically compacted to 10,000 psi. Product collected after the test was checked for size. Detailed data is shown in Table 4.

Resilient graphite rebounded 114% upon pressure release from 10,000 psi. Ground marble, CPC and walnut shell all have very low resiliency. There was practically no size degradation by compressive stress for walnut shell particles as 97.1% remain above 40 mesh. Surprisingly 11.8% of material showed up at 30 mesh screen. In essence, shape of some particles changed during compaction, i.e. flattened, thus effectively became "larger". Ground marble was very brittle. Only 10.3% left on 40 mesh screen after resiliency test, and 70.8% of fines less than 60 mesh were generated. CPC was also rather brittle with 36.7% of original size left after compaction. Electrothermal purification, the manufacturing process that made resilient graphite, apparently makes the product a lot tougher. 81.5% of material was left on 40 mesh after resiliency test.

Attempt was made to test 30/40 walnut shell sample after static aging in water at 300°F. However a solid slug, with apparent density of 0.90 g/cc, was formed instead. All other materials remained in powder form after compressive testing.

The walnut shell medium sample was hot pressed at 4,351psi (30MPa) for 10 minutes at 150°F, 200°F, 250°F and 300°F. Solid slug was formed after hot pressing at 200°F and higher. The solid slug formed at 200°F was rather weak; edges broke off at multiple spots while pushing it out. It became a lot stronger at 250°F, and a very solid piece was formed at 300°F. Apparent density was 1.08 g/cc after hot pressing at 200°F. It increased to 1.21 g/cc after hot pressing at 300°F, or 85% its theoretical density. It appeared that the resinous material may have promoted compaction during hot pressing.

Resilient graphite didn't form a slug in hot pressing.

Single particle compression testing was also conducted for detailed compression behavior. One large particle, about 1-2 mm in length was picked from original sample and placed in between two platens and compressed to a maximum load of 20 Newton for 5 seconds. The top platen moved at a constant speed of 10 μm/s during engagement and 50 μm/s on release. Detailed particle height information during the experiment are shown in Fig. 7. Walnut shell and resilient graphite particles showed very different behavior under compressive stress. Not only did resilient graphite compressed more to the same peak load (24.6% vs. 5.7%), upon pressure release, much higher proportion of its deformation was recovered compared with walnut shell particles (67% vs. 23%). Upon close examination, the top surface of the walnut particle was flattened. In essence, under compressive stress, walnut shell particles experienced mostly plastic/permanent deformation, while majority of resilient graphite deformation was recoverable. Due to different mechanical properties, synergy is expected when used together in the field. For example, resilient graphite addition to nut shell and ground marble treatment was found beneficial on sealing performance [1].

Conclusion

Particulate LCMs commonly used in wellbore strengthening operation (calcined petroleum coke, resilient graphite, ground marble and walnut shell) were investigated in this study on degradation behavior under shear and compressive stress, particularly at elevated temperatures. The following conclusions can be drawn based on experimental observations:

1. Walnut shell can be quite reactive at elevated temperatures. Interaction with water during static aging at 300°F resulted in ~37% weight loss and reduced particle size. Mechanically the product became weaker and degraded more under extreme shear stress.
2. Electro-thermal purification, the manufacturing process used to produce resilient graphite, makes the product a lot stronger compared to CPC.
3. When trapped in between fast-moving surfaces, due to its toughness, walnut shell particles have the potential to cause major damage to metallic surfaces and seals, etc. It is thus recommended to avoid selecting or generating particle size close to those limits in downhole tools, pumps, etc. Walnut shell particles were also found to be the most abrasive among tested samples.
4. Walnut shell and resilient graphite behaved differently under compressive stress. Walnut shell particles experienced mostly plastic/permanent deformation. Resilient graphite deformed a lot more and most of the deformation recovered upon pressure release.

In this study it is confirmed that walnut shell and resilient graphite are two of the best LCM products in resisting degradation by shear and compressive forces. Walnut shell can be very effective in the right environment. Its abrasiveness can be a concern depending on application. Performance degraded at elevated temperature; chemically, it turned more reactive and, mechanically, the structure became weaker. Due to its chemical inertness and excellent thermal stability, resilient graphite provides the best all-around solution.

Acknowledgments

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Graphics

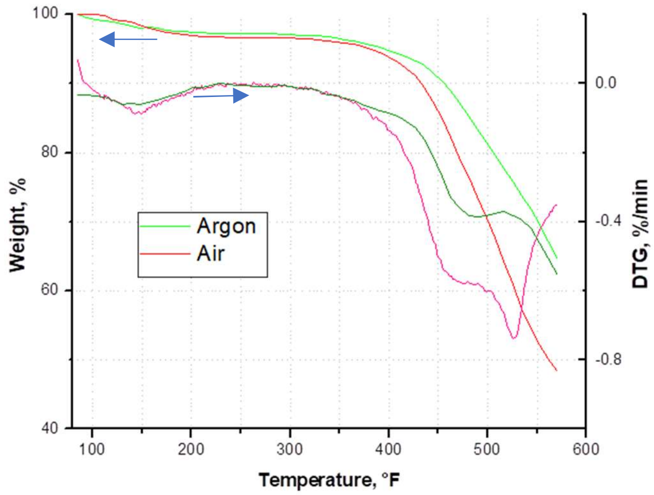

Figure 1. Thermogravimetric Study of 30/40 mesh Walnut Shell sample in Air and Argon atmosphere.

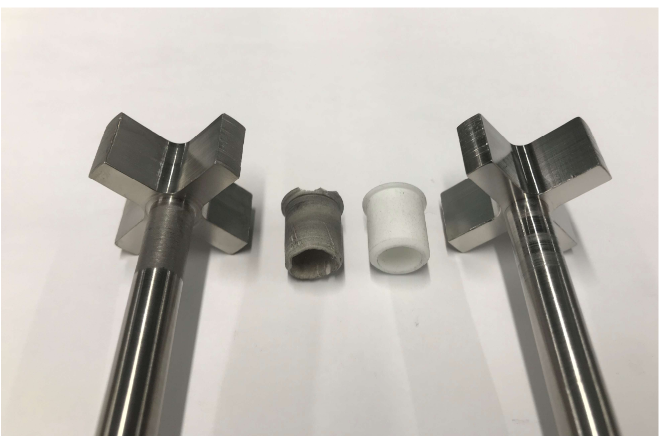

Figure 2. Worn rotor and PTFE bushing after shear degradation testing of walnut shell medium in WBM. Another set of lightly used bushing and rotor were shown (right) for comparison

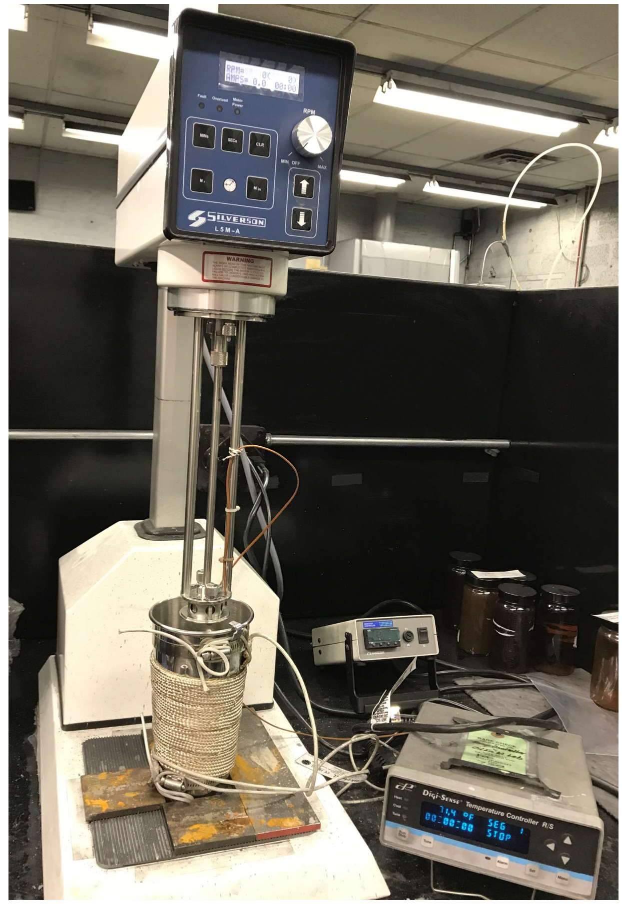

Figure 3. Shear degradation experimental setup for testing at elevated temperatures with in situ heating.

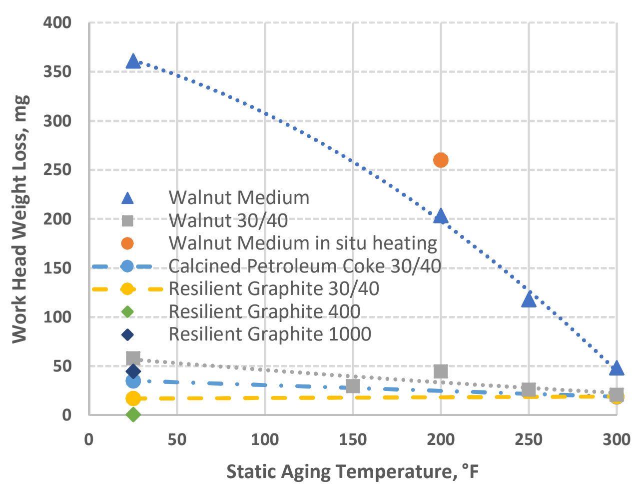

Figure 4. General purpose dispersion head weight loss as a function of static aging temperature. Shear degradation test conducted in weighted bentonite fluid.

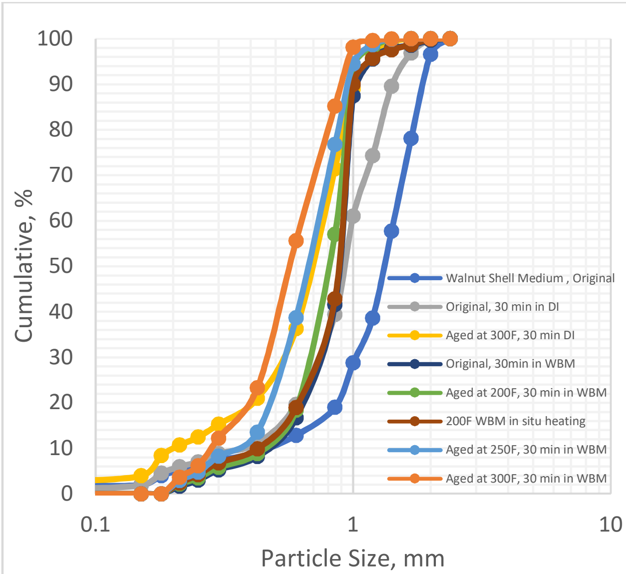

Figure 5. Shear degradation testing of Walnut Shell Medium sample in DI and WBM.

Figure 6. Scratching marks on the inner surface of general purpose disintegration head after shear degradation testing of walnut shell samples. Another lightly used work head was shown (right) for comparison.

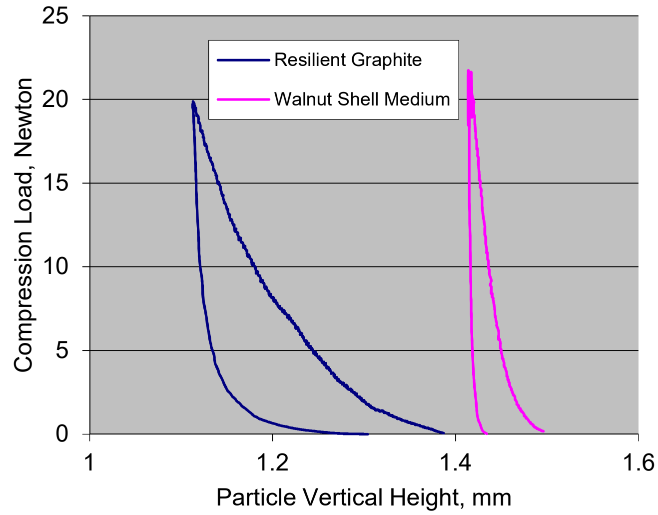

Figure 7. Single particle compression testing

Tables

Table 1. Properties of static aged and dried (250°F, 16 hrs) 30/40 Mesh Walnut Shell in DI water

Static Aging Temperature	**RT**	**150°F**	**200°F**	**250°F**	**300°F**
Weight Loss after Drying@250°F, %	5.8	9.6	10.6	17.2	36.6
Retain above 40 mesh, %	91.5	93.8	90.5	89.7	85.0
Weight above 40 mesh, % of feed	86.2	84.8	80.9	74.0	53.4
BET Surface Area, m^2/g	0.58	0.31	0.42	0.90	7.1
Porosity, cm^3/g	0.0003	0.0003	0.0003	0.0016	0.016
Average Pore Size, nm	3.2	10.6	11.2	6.8	7.4

Table 2. Shear degradation study of 30/40 mesh samples in DI Water.

Sample	Aging Temperature °F	Retains above 40 mesh, %	50-60 mesh, %	-60 mesh, %
Walnut Shell	N/A	75.0	13.6	0.8
Walnut Shell	150°F	78.0	10.2	0.7
Walnut Shell	200°F	73.8	12.2	0.8
Walnut Shell	200°F in situ*	73.0	13.2	1.6
Walnut Shell	250°F	63.0	15.7	1.0
Walnut Shell	300°F	40.4	15.9	1.6
Ground marble	N/A	4.9	7.3	63.6
Calcined Petroleum Coke	N/A	28.1	38.0	29.6
Resilient Graphite	N/A	57.6	32.8	8.9
Resilient Graphite	300°F	55.0	34.1	9.5

Note: Product finer than 325 mesh were not collected. Weight percentage based on starting material.

Table 3. Abrasiveness testing of LCM grades. Test procedure adopted from API RP 13I

Sample	Abrasiveness, mg/min
Resilient graphite 400	0.16
Resilient graphite 1000	0.15
Walnut Shell Fine	1.69

Table 4. Screen Analysis of 30/40 Mesh Samples after Hydraulic Compression (10,000 psi) Testing

Sample	Ground marble	CPC	Resilient Graphite	Walnut Shell
Resiliency, %	3	15	114	18
Retain above 40 mesh, %	10.3	36.7	81.5	97.1
40-60 mesh, %	18.9	22.3	10.1	3.1
-60 mesh, %	70.8	41.0	8.4	0.6