Carbon additives for high-quality well cementing

V S Kovalchuk and N I Nikolaev
Saint Petersburg Mining University, 2, 21st line, Saint Petersburg, 199106, Russian Federation

E-mail: vlada.1995@inbox.ru

Abstract. This article deals with the possibility of adding carbon materials to the cement system. The obtained experimental results are able to analyze the physical and mechanical properties of the grouting mixtures modified with the graphite and its derivatives. The solution of the highly efficient well cementing and fixing operations should be done by the introduction chemical additives to the cement slurry. It is necessary to conduct laboratory investigation with respect to the certain geological, technical and technological features of the mine. That is why several types of carbon additives were examined. The results of this study are useful for finding efficient and ecologically friendly resolution and the maximal strength and minimal permeability values of the grouting mixtures, modified with graphite, oxidized graphite, and flacked thermally expanded oxidized graphite.

1. Introduction
Nowadays we face the problem of the environmental degradation that pushes people to actively search for the most suitable solution. Production facilities are among the most dangerous enterprises not only for workers but also for the environment. Production facilities are among the most dangerous enterprises not only for workers, but also for the environment. Mining enterprises, including drilling companies, meet increased requirements for reducing the load on nature, energy efficient production, and waste disposal. Such new industry requirements are forcing scientists to create modern methods, compositions, and equipment solutions. Cement is used to increase the strength and durability of wells for various purposes. The problem of increasing durability of cement containing materials and increasing of resource-saving production has been solving for years. Oil and gas industry provide a large number of materials for a permanent well casing process. The necessity in sustainable future generates ideas of implementation of different carbon materials for well cementing. Although there is no additive ideal for all conditions, scientists have identified major properties-enhancing chemicals.

Major scientists are looking for a way out in replacing cement with the large amounts of a fly ash or/and limestone [1, 2, 3, 4, 5, 6, 7], to develop a “green cement” without loss of properties required for application. In the articles [8, 9, 10, 11, 12] the structural, rheological, mechanical and physical properties of the cement slurries and concrete modified with a fly ash were investigated. Mixtures of cement with clay are known for its availability and low cost. Calcined clay draw attention to itself only recently. The article [13, 14, 15, 16] expresses the results of laboratory studies of calcined clay as a pozzolan on physical characteristics of the concrete. It was supposed that the using of calcined clays leads to the new low carbon cement, that will help to overcome cement production pollution. In the article [17, 18, 19], cements with the addition of calcined clays were considered. To evaluate the characteristics of the calcined clay cement concrete specimens in the study [20, 21, 22, 23], samples
with the cement replacement were investigated. Rheological and durability features of cements modified with the calcined clay were studied in the work [24, 25, 26]. Oil and gas wells often face such conditions as high pressure and temperature (HPHT) conditions.

After recent discoveries of the new carbon modifications in the form fullerene and graphene carbon materials became popular among all researchers. In the study [27] the efficiency of nanosynthetic graphite to the plugging compositions were tested. It was detected that the addition of 0.5% BWOC of the nanosynthetic graphite was sufficient to get improved compressive strength. The test results of the authors [28, 29] show that inexpensive graphite nanoplatelets are possible to use as a nanoreinforcement of the plugging mixtures. As reported in [30], the presence of Graphene Nano Platelets strongly improves the chemical and physical properties of the cement composition and Long-Term Reliability in Oil Wells. In the research [31], the influence of the Carbon Nanotube on the rheological and physical properties of the cement slurry under high pressure was studied. In the work [32, 33], the effect of the cement modified with multi walled carbon nano tubes in HPHT conditions on its mechanical and thixotropic properties was shown.

The analysis of the significant research studies on the use of chemicals showed a positive result of modifying cements with different additives. Yet the introduction of carbon materials as an additive in concretes and cements is not widely implemented and explored. It is known that the ability of the influence of carbon materials on the quality of the grouting mixtures and cement stones for high-quality well casing exists. The application of different carbon materials requires modern solutions and examinations to find an ECO replacement of the cement or highly efficient modifier to grouting mixtures for waste free production.

2. Materials and methods

The choice of the carbon materials to investigate the plugging slurry was made in favor of graphite (G). This widely used carbon containing material was compared with the oxidized graphite (OG) and flaked thermally expanded oxidized graphite (TOG), obtained by oxidation and thermal expansion in a heater of graphite. The experimental studies included preparing of grouting slurry with composition of alumina cement brand AC-40, technical water and several percentages of carbon additives. The water cement ratio for all cement compositions was 0.5. After preparing investigated mixtures were studied with the help of rheological equipment, afterwards the were placed in the molds 40x40x40 cm for 1, 3, 10 days for hardening under normal temperature and pressure. All the structural and physical parameters of the cement compositions were examined according to the international standard ISO 10426-1 at the laboratory of drilling and grouting fluids, St Petersburg Mining University.

2.1. Grouting mixtures with an addition of graphite

The first cement slurry was made using only alumina cement AC-40 mark and technical water was prepared to compare the difference between pure cement and modified cement in achieved strength parameters. The next five mixtures were made with addition of graphite in quantity [1; 1.5; 2; 2.5; 3] % respectively. The results of the uniaxial compression strength after hardening 1, 3, 10 days in the special metal molds is presented in table 1. The strength test data of the cement stone samples with addition of graphite after 1, 3, 10 days of curing is shown in figure 1.

| Number of sample | 1   | 2   | 3   | 4   | 5   | 6   |
|------------------|-----|-----|-----|-----|-----|-----|
| Uniaxial compression strength in a day, MPa | 7.43 | 6.40 | 6.78 | 6.82 | 6.89 | 6.95 |
| Uniaxial compressive strength after 3 days, MPa | 12.66 | 11.18 | 10.97 | 11.12 | 11.05 | 11.34 |
| Uniaxial compressive strength after 10 days, MPa | 18.58 | 17.41 | 17.36 | 17.5  | 17.61 | 17.69 |
Almost always, when additives are introduced into cement paste, its characteristics deteriorate. Therefore, usually to achieve the required properties, it is necessary to use a complex of additives, for example, plasticizers, retarders or set accelerators, expanding additives, etc. This paper considers the impact of only carbon materials in an amount from 0% to 3%. From the obtained data, it can be concluded that carbon materials have a slight effect on the strength properties of cement stone. Since the studies included the average value over three samples, there is a certain measurement error. To summarize, the introduction of graphite does not impair the strength properties of the cement stone.

![Figure 1. Strength bar chart of the cement stone samples with an addition of graphite.](image)

### 2.2. Plugging mixtures modified with oxidized graphite

The first “control” cement slurry, made from alumina cement and water was compared with the five mixtures with addition of oxidized graphite in quantity [1; 1.5; 2; 2.5; 3] % accordingly. The results of the uniaxial compression strength test data are presented in table 2 and in figure 2.

**Table 2.** Results of the compositions of plugging mixtures modified with oxidized graphite.

| Number of sample | 1    | 2    | 3    | 4    | 5    | 6    |
|------------------|------|------|------|------|------|------|
| Uniaxial compression strength in a day, MPa | 7.43 | 5.79 | 6.13 | 6.59 | 7.09 | 7.30 |
| Uniaxial compressive strength after 3 days, MPa | 12.66 | 10.75 | 10.73 | 11.51 | 12.16 | 12.46 |
| Uniaxial compressive strength after 10 days, MPa | 18.58 | 17.23 | 17.24 | 17.46 | 18.21 | 19.01 |

According to the obtained experimental data and the plotted diagram, with the introduction of a larger amount of oxidized graphite, the physical and mechanical properties of the grouting mixture increase. This is due to the formation of molecular bonds not just of crystalline graphite, but the influence of oxides obtained after acid evaporation [34, 35, 36]. Due to the presence of oxides, micro-reinforcement of the cement matrix occurs and the permeability of the cement stone decreases. With an increase in the addition of OG, a linear increase in the strength of the stone occurs after 1, 3, 10 days.
Figure 2. Strength bar chart of the hardened cement cubes modified with oxidized graphite.

2.3. Modified with flaked thermally expanded oxidized graphite grouting mixtures

The first pure cement slurry, prepared from alumina cement and water was compared with the seven mixtures with addition of thermally expanded oxidized graphite in quantity [0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1] % relatively. The received results of the compression strength test data are shown in table 3 and in figure 3.

Table 3. Results of the modified with thermally expanded oxidized graphite grouting mixtures compositions.

| Number of sample | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Uniaxial compression strength in a day, MPa | 7.43 | 3.70 | 3.61 | 3.82 | 3.85 | 4.55 | 4.92 | 4.87 |
| Uniaxial compressive strength after 3 days, MPa | 12.66 | 6.11 | 6.06 | 6.25 | 6.58 | 7.10 | 7.23 | 7.39 |
| Uniaxial compressive strength after 10 days, MPa | 18.58 | 10.58 | 10.42 | 10.65 | 10.88 | 10.91 | 11.03 | 11.43 |

Figure 3. Strength bar chart of the cured plugging mixtures with a modification of thermally expanded oxidized graphite.
The modification of grouting mixtures with thermally expanded oxidized graphite showed a pronounced decrease in the mechanical properties of the hardened cement mortar. Similarly, to the data of oxidized graphite, with the introduction of a larger amount of TOG, the strength gain of the modified cement stone increases at all stages of hardening. During the heat treatment of oxidized graphite, the material greatly increases in volume, becoming a foam of OG. Due to the critical growth of pores, TOG negatively affects the physical properties of the cement, which makes this additive inactive in comparison with previous samples. The assumption of an increase in the specific surface area and porosity of additives in plugging compositions turns out to be false.

2.4. Computer micro tomography tests of the cement stone

The next step of examining of hard-set cement was a computer micro tomography analysis to evaluate the pore structure and permeability of the pure cement stone (1) and sample with the addition of graphite (2), oxidized graphite (3) and thermally expanded oxidized graphite (4). The received results of the computer micro tomography tests are shown in table 4 and in figures 4, 5, 6.

After the received diagrams, it was determined that the number of closed pores decreases with the introduction of carbon materials. When TOG is introduced, it reaches a minimum and, most likely, this volume is replaced by pores of the foamed OG. In pure cement slurry, the volume of closed pores significantly exceeds the volume of open pores. when graphite is introduced, the values of buried and open pores tend to the same. The addition of oxidized graphite is an intermediate stage between pure cement and cement modified with graphite. However, the total pore volume of the third sample is less than that of its two predecessors. With the addition of TOG, there is a sharp increase in the volume of open pores, and a decrease in the volume of closed pores. This is happening due to the high porosity of the carbon material. An interesting castling of open and closed pores has a negative effect on the strength and permeability properties of the cement stone for wells fixing.

Table 4. Results of the computer micro tomography of the grouting mixtures.

| Additive   | 1   | 2    | 3    | 4    |
|------------|-----|------|------|------|
| Number of closed pores, Po.N(cl), | -   | G    | OG   | TOG |
| Volume of closed pores, Po.V(cl), mm^3 | 7599 | 3743.00 | 4010.00 | 1531.00 |
| Volume of open pore space, Po.V(op), mm^3 | 8.40566 | 4.72699 | 4.80014 | 1.82638 |
| Closed porosity (percent), Po(cl), % | 1.14105 | 2.42265 | 0.68483 | 2.57597 |
| Open porosity (percent), Po(op), % | 0.17253 | 1.09728 | 0.07842 | 8.40805 |

![Figure 4](image_url). Number of closed pores of the cement stones.
After plotting the porosity of the samples, it was determined that the most permeable is sample 4 - with the addition of TOG. The best example with a reduced porosity is a cement modified with oxidized graphite. At the same time the addition of graphite slightly increases the open and closed porosity of the cement stone, which leads to an increase in its permeability.

3. Results
The received results of modification of alumina cement AC-40 brand with graphite and oxidized graphite in an amount of 0.4-3% BWOC showed an insignificant change in physical and mechanical properties, while the addition of thermally expanded oxidized graphite showed a strong decrease in the strength properties of the modified cement stone. It was determined that the larger introduction of OG has an improving positive effect on grouting mixtures. It is necessary to pay special attention to additives to alumina cement AC-40 mark. According to the computer microtomography data, it was shown that the best technological characteristics are achieved when oxidized graphite is incorporated into a cement matrix, and the higher the amount of OG, the better the properties of the solution. The highest porosity was shown by the modified TOG sample, which presents its inefficiency and fragility for high-quality wells construction.
4. Conclusion
Constantly increasing environmental and technological requirements are forcing scientists to find new types of additives that will positively affect the quality of well casing. According to the results of the laboratory tests of the grouting slurries with the addition of graphite and its derivatives, it was determined that the use of alumina cement and thermally expanded oxidized graphite does not show a qualitative industrial implementation. The most successful was a cement mortar with the addition of oxidized graphite in the amount of 3% BWOC. Alumina cement AC-40 mark is a satisfactory material for wells fixing yet not all its features are sufficient for its extensive application for building mines. The introduction of graphite and its derivatives requires primary experimental research. The influence of the complex composition of additives on the resulting plugging mixtures is recommended to be tested according to all environmental, geological and technological requirements of a particular mineral field.

Acknowledgments
The authors would like to acknowledge the Russian Foundation of Basic Researches (154861Y/2020), that provided the financial support as well as the support from Kashurin R R "National Fire Company", with help of that were provided materials, equipment and guidance throughout the research process.

References
[1] Naidu P V and Pandey P K 2014 Replacement of cement in concrete International journal of environmental research and development 4(1) 91-8
[2] Phul A A, Memon M J, Shah S N R and Sandhu A R 2019 GGBS and fly ash effects on compressive strength by partial replacement of cement concrete Civil Engineering Journal 5(4) 913-21
[3] Al-Amoudi O S B, Maslehuddin M and Asi I M 1996 Performance and correlation of the properties of fly ash cement concrete Cement, Concrete and Aggregates 18(2) 71-7
[4] Poon C S, Lam L and Wong Y L 2000 Study on high strength concrete prepared with large volumes of low calcium fly ash Cement and Concrete Research 30(3) 447-55
[5] Cho Y K, Jung S H and Choi Y C 2019 Effects of chemical composition of fly ash on compressive strength of fly ash cement mortar Construction and Building Materials 204 pp 255-64
[6] Elmrabet R, Harfi A and Youbi M S 2019 Study of properties of fly ash cements Materials Today: Proceedings 13(3) 453
[7] Elkhadiri I, Diouri A, Boukhari A, Jalili Aride and Puertas F 2002 Mechanical behaviour of various mortars made by combined fly ash and limestone in Moroccan Portland cement Cement and Concrete Research - CEM CONCR RES 32 1597-603
[8] Wang Z and Song Y 2016 Adsorption properties of CFBC ash–cement pastes as compared with PCC fly ash–cement pastes International Journal of Coal Science & Technology 3 62-7
[9] Termkhajornkit P, Nawa T, Yamashiro Y and Saito T 2009 Self-healing ability of fly ash–cement systems Cement & Concrete Composites 31(3) 195-203
[10] Sengul O and Tasdemir M 2009 Compressive Strength and Rapid Chloride Permeability of Concretes with Ground Fly Ash and Slag Journal of Materials in Civil Engineering - J MATER CIVIL ENG 21(9) 1
[11] Moses P, Chockalingam M P, Venkatakrishnaiah R and Dayakar P 2020 Strength aspects of fly ash in cement mortar International journal of advanced research in engineering & technology 11(1) 38-44
[12] Malolepszy J and Tkaczewska E 2007 Effect of fly ash fineness on fly ash cement hydration and properties Cement Wapno Beton 12(74) 297-302
[13] Adekitan O and Poppoola M 2020 Potentials of calcined clay as a pozzolan Epitoanyag - Journal of Silicate Based and Composite Materials 72(2) 70-1
[14] Amankwah E, Bediako M and Kankam C 2014 Influence of calcined clay pozzolana on strength characteristics of Portland cement concrete International Journal of Material Science and Application 3(6) 410-9
[15] Danner T and Justnes H 2018 The Influence of Production Parameters on Pozzolanic Reactivity of Calcined Clays Nordic Concrete Research 59 1-12

[16] Rasmussen K, Moesgaard M, Kahler L, Tran T and Skibsted J 2015 Comparison of the Pozzolanic Reactivity for Flash and Soak Calcined Clays in Portland Cement Blends RILEM Bookseries 10 151-7

[17] Aramburo C, Pedrajas C, Rahhal V, González M and Talero R 2018 Calcined Clays for low carbon cement: Rheological behaviour in fresh Portland cement pastes Materials Letters 239 24-8

[18] Beunten N and Thienel C 2015 Properties of Calcined Lias Delta Clay - Technological Effects, Physical Characteristics and Reactivity in Cement RILEM Bookseries 10 43-50

[19] Chen Y, Romero Rodriguez C, li Z, Chen B, Çopuroğlu O and Schlangen E 2020 Effect of different grade levels of calcined clays on fresh and hardened properties of ternary-blended cementitious materials for 3D printing Cement and Concrete Composites 114 103708

[20] Lemma R, Irassar E and Rahhal V 2015 Calcined Illitic Clays as Portland Cement Replacements RILEM Bookseries 10 269-76

[21] Marangu J M, Karanja T and Muthengia J 2018 Properties of activated blended cement containing high content of calcined clay Heliyon 4(8) 1

[22] Oliveira M P and Barbosa N P 2006 Potentialities of a calcined kaolin as material of partial replacement of portland cement in mortars Rev. bras. eng. agric. ambient 10(2) 490-6.

[23] Toledo Filho R D, Americano B B, Fairbairn E M R, Rolim J S and Filho J F 2007 Potential of Crushed Waste Calcined-Clay Brick as a Partial Replacement for Portland Cement Sustainable development of cement and concrete 202 147-60

[24] Irassar E, Rahhal V, Pedrajas C and Talero R 2014 Rheology of portland cement paste with calcined clays additions Technical Proceedings of the 2014 NSTI Nanotechnology Conference and Expo, NSTI-Nanotech 3 234-7

[25] Pierkes R, Schulze S and Rickert J 2018 Durability of Concretes Made with Calcined Clay Composite Cements Calcined Clays for Sustainable Concrete 16 366-73

[26] Sposito R, Thienel C and Beunten N 2016 Influence of aging conditions upon the properties of calcined clay and its performance as supplementary cementitious material Cement and Concrete Composites 72 114-24

[27] Shawgi A, Chinedum P E and Saeed S 2018 Improvement in Cement Sealing Properties and Integrity Using Conductive Carbon Nano Materials: From Strength to Thickening Time SPE Annual Technical Conference and Exhibition, 24-26 September, Dallas, Texas, USA

[28] Peyvandi A, Taleghani, A D, Soroushian P and Cammarata, R 2017 The Use of Low-Cost Graphite Nanomaterials to Enhance Zonal Isolation in Oil and Gas Wells SPE Annual Technical Conference and Exhibition, 9-11 October, San Antonio, Texas, USA

[29] Tabatabaei M, Taleghani A D and Alem N 2019 Economic Nano-Additive to Improve Cement Sealing Capability SPE Western Regional Meeting, 23-26 April, San Jose, California, USA

[30] Alkhamis M and Imqam A 2018 New Cement Formulations Utilizing Graphene Nano Platelets to Improve Cement Properties and Long-Term Reliability in Oil Wells SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition

[31] Al-Awami A H 2018 Carbon Nanotube Under High Pressure SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition, 23-26 April, Dammam, Saudi Arabia

[32] Rahman M K, Khan W A, Mahmoud M A and Sarmah P 2016 MWCNT for Enhancing Mechanical and Thixotropic Properties of Cement for HPHT Applications Offshore Technology Conference Asia, 22-25 March, Kuala Lumpur, Malaysia

[33] Khan W A, Rahman M K, Mahmoud M A and Sarmah P 2016 MWCNT for Enhancing Mechanical Properties of Oil Well Cement for HPHT Applications SPE/IADC Middle East Drilling Technology Conference and Exhibition, 26-28 January, Abu Dhabi, UAE

[34] Lojka M, Lochman B, Jankovský O, Jiřičková A, Sofer Z and Sedmidubský D 2019 Synthesis, Composition, and Properties of Partially Oxidized Graphite Oxides Materials 12 2367
[35] Ciszewski M and Mianowski A 2014 Capacitive behavior of highly-oxidized graphite *Materials Science-Poland* **32** 307-14

[36] Zhang G, Wen M, Wang S and Wang J 2018 Insights into thermal reduction of the oxidized graphite from the electro-oxidation processing of nuclear graphite matrix *RSC Advances* **8** 567-79