Thermodynamic calculations on system «Portland cement – water – carbon nanomodifier»

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Abstract. The article presents the results of thermodynamic modelling in a cement-water-carbon nanomodifier system. A carbon nanomodifier contains fullerenes C₆₀ and C₇₀. Thermodynamic calculations make it possible to evaluate the contribution of a carbon nanomodifier to the hydration process of Portland cement. Using thermodynamic calculations, changes in the phase composition and general properties of the system (total enthalpy, entropy) with the introduction of a carbon nanomodifier were determined.

1. Introduction
Research is relevant for improving the properties of cement composites using carbon-type modifying additives [1-4]. Modifying additives containing carbon and allotropic forms of carbon (fullerenes, nanotubes, fulleroid particles) can improve the properties of the cement composite at small amounts: 0.001 mass% - 0.1 mass%. Modified composites have improved strength characteristics, increased frost resistance properties. The use of carbon nanomodifiers in the future will reduce cement consumption in the production of concrete various classes. The effect of using carbon nanomodifier (CNM) depends on the type and composition of the additive, since allotropic forms of carbon have different physicochemical and adsorption properties. One of the explanations for the effect of using carbon nanomodifiers is the effect of nanomodifiers on kinetics of cement stone hydration, changes in phase composition, and changes in the heat release of cement dough during hydration. The change in thermophysical properties can be determined experimentally (for example, by the calorimetric method) and theoretically, by the method of thermodynamic modeling.

Thermodynamic modeling (TM) is a universal research method. When creating new composite materials and developing new effective, resource-efficient and energy-efficient methods of synthesis, TM is used. The main task of thermodynamic modeling is to determine phase and chemical composition of the system and values of thermodynamic properties of the system. Thermodynamic data allow us to assess the possibility of processes in terms of thermodynamics.

There are many programs for thermodynamic modeling [5,7]. For example, the interactive GEMS-Selektor package for thermodynamic modeling of water (geo) chemical systems by Gibbs Energy Minimization [5-6]. The interactive GEMS-Selektor package can be used in various fields of science depending on the database, particularly in construction chemistry.

In this paper, we used the multi-purpose software package TERRA [8]. Thermodynamic modeling is an important step in creation of composite materials, their production processes, and hydration of the source components. Terra software for calculating chemical reactions uses equilibrium conditions:
Gibbs energy minimization and entropy maximum condition. In the first case, the optimization problem presented by the conditions $\Delta G^o_{\text{reaction}} \to \min; \sum_{q} C_{ij} X_j \leq b_j$, where $b_j$ a certain amount of interacting chemical element $B_j; X_j$ - stoichiometric coefficient of the compound, $C_{ij} C_{ij}$ - number of Bi atoms in compound j, N - number of chemical elements involved in the reaction; n - number of reaction products.

In the second case, the calculation is based on the maximum entropy conditions $\max S \to S_{\text{max}}$, constancy of the total internal energy, fulfillment law of conservation mass of all chemical elements [8, 9].

In the problem of thermodynamic modeling, two conditions of equilibrium with the environment were assigned. These conditions can be either numerical values of the thermodynamic characteristics of the equilibrium, or functional relations between the parameters of this state. To describe a system as a material object, it is necessary to know the content of the chemical elements that form it. Internal and interfacial interactions are described by model thermodynamic relations, which are closed using the properties of only individual substances-components of equilibrium.

2. Experimental part
In this paper we used the interfaces of the TERRA software package:

1. **TERRA.** The maximum number of chemical elements that can make up the system under study is 50; the number of condensed phases considered in a single calculation is limited to 200, and the number of components of the gas phase formed in equilibrium (the number of individual substances) can reach 800. When performing calculations for heterogeneous systems, it is possible to use a model of single-component immiscible phases and models of condensed solutions.

2. **INFO.** The INFO helper program is designed to serve the TERRA database. The INFO database contains the thermodynamic data of substances for calculating chemical and thermodynamic equilibrium of arbitrary multicomponent systems.

For thermodynamic calculations hydration of Portland cement in the database of the TERRA software complex (INFO program) were added:

- fullerences $C_{60}$ and $C_{70}$, Table 1 [10],
- fullerence $C_{60}$ hydrides [11],
- thermodynamic properties of substances involved in the hydration process, Table 2 [12-14]

### Table 1. Thermodynamic properties of fullerenes

| Fullerene | $\Delta_f H^0$ (kJ/mol) | $S^0$ (J/K/mol) | $a_0$ | $a_1$ | $a_2$ | $a_3$ |
|-----------|-------------------------|----------------|-------|-------|-------|-------|
| $C_{60}$  | 2346                    | 427.1          | -292.4| 3.43  | -0.025| 6.36 $\times 10^{-7}$ |
| $C_{70}$  | 2555                    | 452.7          | -295.03| 3.78  | -0.0025| 5.39 $\times 10^{-7}$ |
| $C_{60}H_2$ | 2280                  | 395.8          | -424.44| 4.23  | -0.0034| 1.05 $\times 10^{-6}$ |
| $C_{60}H_{18}$ | 1561                 | 437.9          | -507.17| 4.74  | -0.0036| 1.06 $\times 10^{-6}$ |
| $C_{60}H_{60}$ | 1869                 | 745            | -640.67| 5.54  | -0.032| 6.85 $\times 10^{-7}$ |

In Table 1 $a_0, a_1, a_2, a_3$ are the empirical coefficients of the heat capacity function: $C_p = a_0 + a_1 T + a_2 T^2 + a_3 T^3$; $\Delta_f H^0$ - enthalpy of formation at 298 K; $S^0$ - entropy at 298 K [10].

### Table 2. Thermodynamic properties of substances added to the TERRA program database


| Material                  | $\Delta H^\circ$ (kJ/mol) | $S^\circ$ (J/K/mol) | $a_0$ (J/mol) | $a_1$ (J/mol K) | $a_2$ (J/K mol) | $a_3$ (J/K$^{0.5}$/mol) | $V^\circ$ (cm$^3$/mol) |
|--------------------------|--------------------------|---------------------|--------------|----------------|-----------------|--------------------------|------------------------|
| **AFt-phases**           |                          |                     |              |                |                 |                          |                        |
| (Al)-ettringite          | -17535                   | 1900                | 1939         | 0.789          | -               | -                        | 707                    |
| C$_6$As$_3$H$_9$         | -16950                   | 1792.4              | 1452         | 2.156          | -               | -                        | 708                    |
| C$_6$As$_4$H$_{13}$      | -11530.3                 | 1960.4              | 970.7        | 1.483          | -               | -                        | 411                    |
| C$_6$As$_5$H$_{19}$      | -10643.7                 | 646.6               | 764.3        | 1.638          | -               | -                        | 361                    |
| Tricarboaluminate        | 16792                    | 1858                | 2042         | 0.559          | -7.78 $\times$ 10$^6$ | -                        | 650                    |
| Fe-ettringite            | -16600                   | 1937                | 1922         | 0.855          | 2.02 $\times$ 10$^6$ | -                        | 717                    |
| **Hydrogarnet**          |                          |                     |              |                |                 |                          |                        |
| C$_3$AH$_6$              | -5537.3                  | 422                 | 290          | 0.644          | -3.25 $\times$ 10$^6$ | -                        | 150                    |
| C$_3$As$_{0.41}$H$_{6.18}$ | -5699                   | 399                 | 310          | 0.566          | -4.37 $\times$ 10$^6$ | -                        | 146                    |
| C$_3$As$_{0.8}$H$_{6.32}$ | -5847                   | 375                 | 331          | 0.484          | -5.55 $\times$ 10$^6$ | -                        | 142                    |
| C$_3$FH$_6$              | -4518                    | 870                 | 330          | 1.237          | -4.74 $\times$ 10$^6$ | -                        | 155                    |
| **Al-Fe siliceous hydrogarnet (solid solution)** |                 |                     |              |                |                 |                          |                        |
| C$_3$F$_{0.8}$H$_{6.32}$ | -4823                    | 840                 | 371          | 0.478          | -7.03 $\times$ 10$^6$ | -                        | 149                    |
| C$_3$A$_{0.5}$F$_{0.5}$H$_{6.32}$ | -5335                   | 619                 | 367          | 0.471          | -8.10 $\times$ 10$^6$ | -                        | 146                    |
| C$_3$F$_{1.3}$H$_{3.32}$ | -4994                    | 820                 | 395          | 0.383          | -8.39 $\times$ 10$^6$ | -                        | 145                    |
| **AFm-phases**           |                          |                     |              |                |                 |                          |                        |
| C$_4$AH$_{19}$           | -10017.9                 | 1120                | 1163         | 1.047          | -               | -1600                    | 369                    |
| C$_4$AH$_{13}$           | -8262.4                  | 831.5               | 208.3        | 3.13           | -               | -                        | 274                    |
| C$_4$AH$_{11}$           | -7656.6                  | 772.7               | 0.0119       | 3.56           | 1.34 $\times$ 10$^7$ | -                        | 257                    |
| C$_4$AH$_{7.5}$          | -5277.5                  | 450                 | 323          | 0.728          | -               | -                        | 180                    |
| CAH$_{10}$              | -5288.2                  | 610                 | 151          | 1.113          | -               | 3200                    | 193                    |
| C$_4$As$_{0.3}$H$_{12}$  | -8270                    | 713                 | 664          | 1.014          | -1.30 $\times$ 10$^6$ | -800                     | 285                    |
| C$_4$As$_{0.3}$H$_{10.5}$ | -7813.3                  | 668.3               | 0.0095       | 2.836          | 1.07 $\times$ 10$^7$ | -                        | 261                    |
| C$_4$As$_{0.3}$H$_{9}$   | -7349.7                  | 622.5               | 0.0088       | 2.635          | 9.94 $\times$ 10$^8$ | -                        | 249                    |
| C$_4$Ach$_{11}$          | -8250                    | 657                 | 618          | 0.928          | -2.59 $\times$ 10$^6$ | -                        | 262                    |
| C$_4$Ach$_{9}$           | -7618.6                  | 640.6               | 192.4        | 2.042          | -               | -                        | 234                    |
| C$_4$As$_{0.5}$H$_{16}$  | -9930.5                  | 975.0               | 636          | 1.606          | -               | -                        | 351                    |
| C$_4$As$_{0.5}$H$_{14}$  | -9321.8                  | 960.9               | 1028.5       | -              | -               | -                        | 332                    |
| C$_4$As$_{0.5}$H$_{12}$  | -8758.6                  | 791.6               | 175          | 2.594          | -               | -                        | 310                    |
| C$_4$As$_{0.5}$H$_{10.5}$ | -8311.9                  | 721                 | 172          | 2.402          | -               | -                        | 282                    |
| C$_4$As$_{0.5}$H$_{9}$   | -7845.5                  | 703.6               | 169          | 2.211          | -               | -                        | 275                    |
| C$_4$ASH$_{8}$           | -6360                    | 546                 | 438          | 0.749          | -1.13 $\times$ 10$^6$ | -800                     | 216                    |
| C$_4$ASH$_{7}$           | -6066.8                  | 487.6               | 0.0063       | 1.887          | 7.12 $\times$ 10$^8$ | -                        | 215                    |
| C$_4$ASH$_{5.5}$         | -5603.4                  | 454.8               | 0.0057       | 1.685          | 6.36 $\times$ 10$^8$ | -                        | 213                    |
| C$_4$As$_{0.5}$ClH$_{12}$ | -8472                    | 820                 | 557          | 1.414          | -1.02 $\times$ 10$^6$ | 751                      | 289                    |
| C$_4$ACl$_{3}$H$_{10}$   | -7604                    | 731                 | 498          | 0.895          | -2.04 $\times$ 10$^6$ | 1503                     | 272                    |
| C$_4$A(NO$_3$)$_2$H$_{10}$ | -7719.3                  | 821                 | 580          | 1.02           | -2.77 $\times$ 10$^6$ | 872                      | 296                    |
| C$_4$A(NO$_3$)$_2$H$_{10}$ | -7493.1                  | 799                 | 565          | 0.99           | -2.24 $\times$ 10$^6$ | 703                      | 275                    |
| C$_4$FH$_{13}$           | -7435                    | 630                 | 694          | 1.113          | 2.02 $\times$ 10$^6$ | 1600                     | 286                    |
| C$_4$Fe$_{0.3}$H$_{10}$  | -6581                    | 1270                | 308          | 1.201          | -9.08 $\times$ 10$^5$ | 3200                     | 273                    |
| C$_4$F$h_{12}$           | -7485                    | 1230                | 612          | 1.157          | -5.73 $\times$ 10$^5$ | -                        | 292                    |
| C$_4$FsH$_{12}$          | -7662                    | 1430                | 577          | 1.234          | 2.02 $\times$ 10$^6$ | -                        | 321                    |
In Table 2, \( a_0, a_1, a_2, a_3 \) are the empirical coefficients of the heat capacity function: 
\[
C_p = a_0 + a_1T + a_2T^{-2} + a_3T^{-0.5} ; \quad \langle\rangle = 0.
\]
Cement shorthand notation is used: \( A = Al_2O_3; \) \( C = CaO; \) \( F = Fe_2O_3; \) \( H = H_2O; \) \( M = MgO; \) \( S = SiO_2; \) \( c = CO_2; \) \( s = SO_3 \). [12]

In our research, we used Portland cement (PC) “Timlyui Cement Plant” (Republic of Buryatia, Russian Federation). [16] The initial chemical composition of Portland cement is shown in Table 3. Thermodynamic calculations were carried out in the range of 273-573 K, the amount of CNM was 0.001 wt\%, 0.01 wt\%, 0.1 wt\%, and the amount of water was 30%.

### Table 3. Initial composition of Portland cement (PC).

| Oxides   | Content wt % |
|----------|--------------|
| SiO_2    | 21.5         |
| Al_2O_3  | 4.92         |
| CaO      | 65.4         |
| Fe_2O_3  | 4.27         |
| MgO      | 1.06         |
| K_2O     | 0.2          |
| SO_3     | 2.57         |

3. Results and discussion

General properties (enthalpy, entropy, heat capacity) and phase composition changes with temperature were determined. An analysis of the properties dependence in certain temperature ranges were founded sharp changes. This can attributed to phase and chemical transformations associated with the formation of new or intermediate compounds. The increase in enthalpy and entropy with the addition of CNM in the cement-water system can explain by the influence of CNM on the heat release of the cement paste.
Thermodynamic calculations describes exothermic reactions and thermal effects in the cement - water - CNM system and connected the cement hydration in the presence of CNM.

![Enthalpy](image)

**Figure 1.** Enthalpy in system PC - water - CNM

The degree of cement hydration can be determined in various ways by measuring: the amount of Ca(OH)$_2$ in cement paste; heat during hydration; specific gravity of cement paste; amount of chemically bound water; the amount of unhydrated cement (using X-ray diffraction analysis), as well as indirectly by the strength of the cement stone [17]. The calculations performed in the program and experimental data [15, 16] on the study of the properties of modified composites using carbon nanomodifier, allow us to evaluate the efficiency of using fullerenes C$_{60}$ and C$_{70}$ as a modifying additive. The amount of Ca(OH)$_2$ phase varies depending on the amount of CNM in the cement-water system as shown by thermodynamic calculations. The change in the yield of calcium hydroxide shows that the carbon nanomodifier acts as an additive-retarder of cement dough setting. Setting is the transition of cement dough from liquid state to solid state. The effect of such additives is estimated by the amount of Ca(OH)$_2$ in the liquid phase of hydrated cement. Increasing the pH of liquid phase cement dough is the effect of such additives [17]. Experimental study of rheological characteristics was presented in [16].

**Table 4.** Compressive strength of cement stone

| Composition | 7 days of hardening | 28 days of hardening |
|-------------|---------------------|----------------------|
| Control     | 40                  | 61                   |
| CNM 0,01%   | 38                  | 67                   |
| CNM 0,001%  | 44                  | 82                   |
Carbon nanomodifier effect on hydration and kinetics of cement hydration, depending on the amount of carbon nanomodifier. The effect of cement stone modification is shown by thermodynamic calculations and experimental strength data of modified cement stone.

The modification of cement stone helps to deepen the hardening processes, starting from the first hours from the beginning of mixing. The introduction of CNM leads to an increase in the duration of the induction period with subsequent acceleration of the increase in strength. After the initial hardening period (7 days), the strength of the modified cement stone is formed at an increasing rate and by 28 days of hardening exceeds the strength of the control sample by 30% [16].
4. Conclusion
Thermodynamic calculations performed in the TERRA program made it possible to evaluate the effect of CNMs on the hydration of Portland cement. The calculation results are consistent with experimental data and confirm the assumption that CNM has a positive effect on the strength of cement stone by various effects. Thermodynamic calculations made it possible to evaluate the effect of CNM on the process of hydration of Portland cement and the effect of CNM on exothermic reactions in system Portland cement-water-CNMs. Thermodynamic modelling can be successfully used to study modification of cement composites with carbon nanomodifiers or other various additives that improve the properties of the cement composite.

5. References
[1] De Ibarra Y S, Gaitero J J and Campillo I 2006 Atomic force microscopy and nanoindentation of cement pastes with nanotube dispersions. *Phys. Status Solidi A* **203** pp. 1076-1081.
[2] Li G Y, Wang P M, and Zhao X 2005 Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes. *Carbon* **43** pp. 1239-1245.
[3] Falikman V R and Weiner A Ya 2015 New highly effective nano-additives for photocatalytic concretes: synthesis and research. *Nanotechnologies in construction*, **7** (1) pp. 1828.
[4] Artamonova O V and Sergutkina O R 2013 Construction Nanomaterials: Trends of Development and Prospects. *Scientific Bulletin of Voronezh State Architectural and Construction University* **6** pp. 13-23.
[5] Kulik D A, Wagner T, Dmytryeva S V , Kosakowski G, Hingerl F F, Chudnenko K V , and Berner U R 2013 GEM-Selektor geochemical modeling package: revised algorithm and GEMS3K numerical kernel for coupled simulation codes. *Computational Geosciences* **17** (1) 1-24.
[6] Wagner T, Kulik D A, Hingerl F F, and Dmytryeva S V 2012 GEM-Selektor geochemical modeling package: TSolMod library and data interface for multicomponent phase models. *The Canadian Mineralogist* **50** (5), 1173-1195.
[7] Belov G V, Iorish V S, and Yungman V S 2000 Simulation of equilibrium states of thermodynamic systems using IVTANTERMO for Windows. *High Temperature*, **38** (2) 191-196.
[8] Trusov B G 2012 Code System for simulation of phase and chemical equilibriums at higher temperatures Engineering Journal: Science and Innovation 1 240-9

[9] Trusov, B G 2002 Program system TERRA for simulation phase and thermal chemical equilibrium. Proc. XIV Intern. Symp. on Chemical Thermodynamics 483-484

[10] Diky V V, Kabo G J, 2000 Thermodynamic properties of C60 and C70 fullerenes Uspekhi Khimii 69 (2) 107–117

[11] Karpushenkava L S, and Kabo G Y 2008 The thermodynamic properties of fullerene hydrides C60H2. Russian Journal of Physical Chemistry A 82 (7) 1170-1174.

[12] Lothenbach B, Kulik D A, Matschei T, Balonis M, Baquerizo L, Dilnesa B, Miron G D and Myers R J 2019 Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated materials. Cement and Concrete Research 115 472-506.

[13] Dilnesa B Z, Lothenbach B, Renaudin G, Wichser A, Kulik D 2014 Synthesis and characterization of hydrogarnet Ca3(AlxFe1-x)2(SiO4)y(OH)4(3-y). Cement and Concrete Research 59 96-111

[14] Winnefeld F and Lothenbach B 2016 Phase equilibria in the system Ca4Al6O12SO4–Ca2SiO4–CaSO4–H2O referring to the hydration of calcium sulfoaluminate cements RILEM Technical Letters 1 10-6

[15] Semenov A P, Smirnyagina N N, Urkhanova L A, Kanakin S V, Lkhasarano S A, Semenova I A, Dasheev D E, Tsyrenov B O and Khaltarov Z M 2017 Reception carbon nanomodifiers in arc discharge plasma and their application for modifying of building materials IOP Conference Series: Materials Science and Engineering 168 (1) 012059

[16] Smirnyagina N N, Semenov A P, Tsyrenov B O, Dasheev D E, and Khaltarov Z M 2016 Plasma-chemical synthesis of carbon nanotubes and fullerenes to create frost-resistant composite building materials. International Congress on Energy Fluxes and Radiation Effects 356-356.

[17] Pukharenko Yu V, Ryzhov D I and Staroverov V D 2017 Peculiar properties of structural formation of Cement Composites in the Presence of Fueled Type Carbon Nanoparticles Proc. of Moscow State University of Civil Engineering (Moscow: Vestnik MGSU) 12 7 (106) 718–23

[18] Kozlova V K, Karpova Y V, and Volf, A V 2006 Evaluation effectiveness of additives that slow down the setting of cement dough. Polzunovskij vestnik 2 230

[19] Melekhov E S and Shlepnev O K 2018 Development and reconstruction of district water supply systems Proceedings of Universities. Investment. Construction. Real estate 8(4) pp 114–127 DOI: 10.21285/2227-2917-2018-4-114-127

[20] Matveeva M 2018 Synchronization of the activity of participants during the implementation of housing construction projects Proceedings of Universities. Investment. Construction. Real estate 8 pp 31-41 DOI: 10.21285/2227-2917-2018-2-31-41.

[21] Kazimirov I A and Peshkov V V 2019 Determination of price behaviour in the secondary residential real estate market using a multidimensional regression model Proceedings of Universities. Investment. Construction. Real estate 9(3) pp 476–487 DOI: 10.21285/2227-2917-2019-3-476-487