CRACK MODEL IN GRAPHENE CONCRETE

Yurov V.
Candidate of Physics and Mathematics Sciences, Associate Professor
KarTU, Karaganda, Kazakhstan
Zhangozin K.
Candidate of Physics and Mathematics Sciences, Associate Professor,
TSK Vostok LLP, Astana, Republic of Kazakhstan
Kargin D.
Candidate of Physical and Mathematical Sciences, Associate Professor
NAO "L.N. Gumilyov Eurasian National University",
Astana, Kazakhstan
https://doi.org/10.5281/zenodo.13619789

Abstract

A model of nanocracks in concrete is proposed. The length of a nanocrack is taken as the thickness of the surface layer of a solid, which is from 1 to 6 nm for metals and about 60 nm for standard concrete, i.e. it represents a nanostructure. For standard concrete: L_{nm} = 60 nm; $L_{\mu m}$ = 6 microns; L_C = 0.6 mm. These data are typical without external load, without changing the environment. The number of cracks in concrete in the nanostructure region I is 10^5, in the mesoscopic region II is 10^7 and in the pre-destruction region III is about 10^9. Adding graphene and graphene oxide to the cement mortar significantly strengthens (by 4-5 times) standard concrete and reduces the number of nanocracks.

Keywords: model, concrete, cement, nanocrack, nanostructure, graphene.

Introduction

Cracks in concrete, which determine their durability, have been studied for a very long time. Theoretical and experimental methods for studying cracks in concrete can be found in recent dissertations, monographs and reviews [1-9]. But none of them talk about nanocracks, their length and their further development, up to the destruction of concrete.

In minerals, the formation of nanocracks was recently discovered in works [10, 11] using the fractoluminescence method. The essence of the method is that when a mineral is destroyed, atomic bonds on the surface are broken and a luminescence signal appears within 1 to 2 nanoseconds. In this case, surface dislocations create primary nanocracks with a length of 10 to 30 nm. In works [12, 13], we proposed a model for the formation of nanocracks in metals and alloys. The essence of this model is that the surface layer of a metal (like all solids) is a nanolayer (1 to 6 nm in size for a metal), the properties of which differ from the properties of the bulk phase. The surface layer of a solid leads to the formation of nanocracks and the destruction of structural materials.

The purpose of this article is to propose a model for the formation of nanocracks in standard concrete, the kinetics of their development up to its destruction.

Nano cracks in concrete

Concrete consists of cement paste, which is a porous and hierarchical material with different phases. When cement powder is mixed with water, the hydration reaction results in the formation of the main chemical products: calcium silicate hydrate (C–S–H), calcium hydroxide (CH), ettringite, and monosulfoaluminates. C–S–H accounts for approximately 70% of the fully hydrated products and is the main contributor to the mechanical strength of the material [14]. The silicate phases react with water to form calcium hydroxide and a rigid calcium silicate hydrate gel, the C–S–H gel [15]:

$$2(3CaO \cdot SiO_2) + 6H_2O = 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 \quad (1)$$

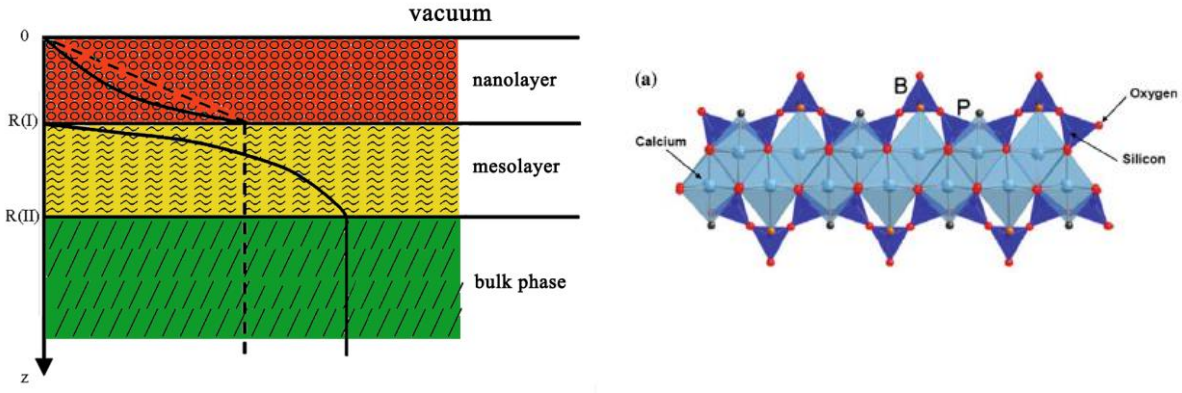
$$2(2CaO \cdot SiO_2) + 4H_2O = 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \quad (2)$$

The thickness of the surface layer of a solid R(I) and the length of nanocracks L_{nm} are given by the formula [16]:

$$R(I) = L_{nm} = 0{,}17 \cdot 10^{-9} \cdot \alpha \cdot \upsilon \, [m]. \quad (3)$$

In equation (3) it is necessary to know one parameter – the molar volume of the element, which is equal to $\upsilon = M/\rho$ (M is the molar mass, ρ is its density), $\alpha = 1$ m^{-2} is a constant to maintain the dimensionality (R(I) [m]). Considering that the rigid calcium silicate gel of the C–S–H hydrate is a homogeneous solid solution, it is easy to estimate the molar mass from equations (1) and (2) – M_1 = 1070 g/mol; M_2 = 922 g/mol. The crystal structure obtained from equation (2) is closer to the mineral tobermorite [17], which is a layered crystalline form of calcium silicate. The density of the C–S–H gel is closely related to the water content in the pores of the gel. Neutron and X-ray scattering methods were used to determine with high accuracy [18] the density and water content of saturated globules. The density is 2.604 g/cm^3,

The thickness of the surface layer of the C–S–H gel according to equation (3) is equal to – L_{nm} = R(I) = 60.3 nm, and the number of layers is n = R(I)/a (a is the interlayer distance, equal to a = 1.4 nm [15]). This means that the number of C–S–H layers is n = 43. According to our work [16], the diagram of the crystalline form of calcium silicate will look like that shown in Fig. 1a, and the silicate chain (monolayer of calcium silicate) is shown in Fig. 1b.



a) *b)*

Figure 1. Scheme of a solid: nanolayer → mesolayer → bulk phase (a); scheme of the C–S–H layer showing the Ca–O core layer with a silicate tetrahedron attached on both sides. The silicate chain, calcium octahedron and oxygen atoms are shown as dark blue, light blue tetrahedron and red spheres, respectively (b) [15].

The thickness of the surface gel layer and the length of the C–S–H nanocracks are equal to L_{nm} = R(I) = 60.3 nm (< 100 nm), i.e. it represents a nanostructure according to Gleiter [19]. The length of the nanocrack in equation (3) reflects the feature that it is associated not only with the geometry of the crystal lattices, but also with the physical properties of the crystals, namely: the type of chemical bond; porosity, anisotropy and other properties. If we consider Fig. 1a, then in work [13] we showed that the evolution of nanocracks occurs according to the law:

$$L_C = 10^2 L_{\mu m} = 10^4 L_{nm} = 0{,}17 \cdot 10^{-5} \cdot M / \rho [\check{e}\,]. \quad (4)$$

where L_{nm}, $L_{\mu m}$, L_C – length of nanocracks, mesocracks and critical length of cracks before destruction of a solid.

So, for standard concrete: L_{nm} = 60 nm; $L_{\mu m}$ = 6 microns; L_C = 0.6 mm. These data are typical without external load, without changes in the environment (temperature, humidity, etc.). Fig. 2 shows the kinetic diagram of fatigue destruction of artillery barrels [20] (in our case, concrete). In this case, the initial and last sections represent a linear function.

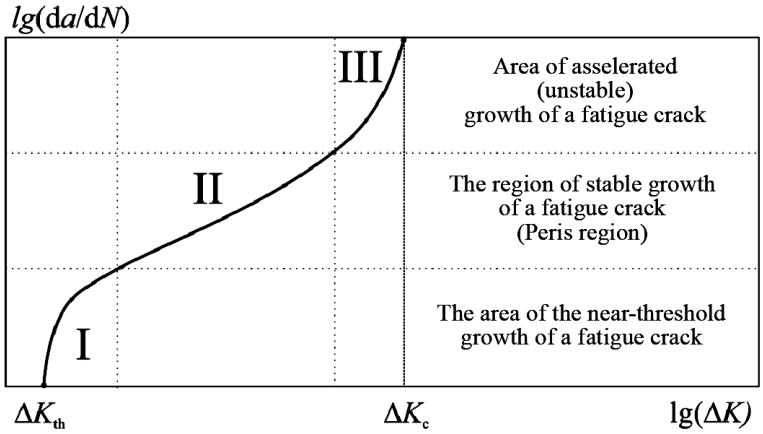


Figure 2. Kinetic diagram of concrete destruction [20].

The diagram shown in Fig. 2 is an S-curve, similar to the line from the theory of catastrophes [21]. If we take the function L(N) as the coordinate of the concrete destruction process, where N is the number of cracks, and select the density of concrete and G/F(I) as the control parameters, where G is the shear modulus (G = 65 GPa for concrete), F(I) is the Peierls-Nabarro barrier (F(I) = 76 10^{-9} Pa for concrete), then we obtain the equation:

$$L(N) = 0.25N^4 - 0.5\rho N^2 - G / F(I) \cdot N. \quad (5)$$

Let us move on to a dynamic system in equation (5), that is, we will consider the crack as a gradient function:

$$\frac{dL(N)}{dt} = \frac{\partial L(N)}{\partial N} = N^3 - \rho N - G / F(I) = 0. \quad (6)$$

Equation (6) is analytically similar to the equation of classical mechanics for the motion of a body in a viscous friction medium. The process of transition from one state to another is smooth, similar to an S-shaped curve (Fig. 2). Calculating equation (6) using Cardan's formula, we obtain for the number of cracks in concrete

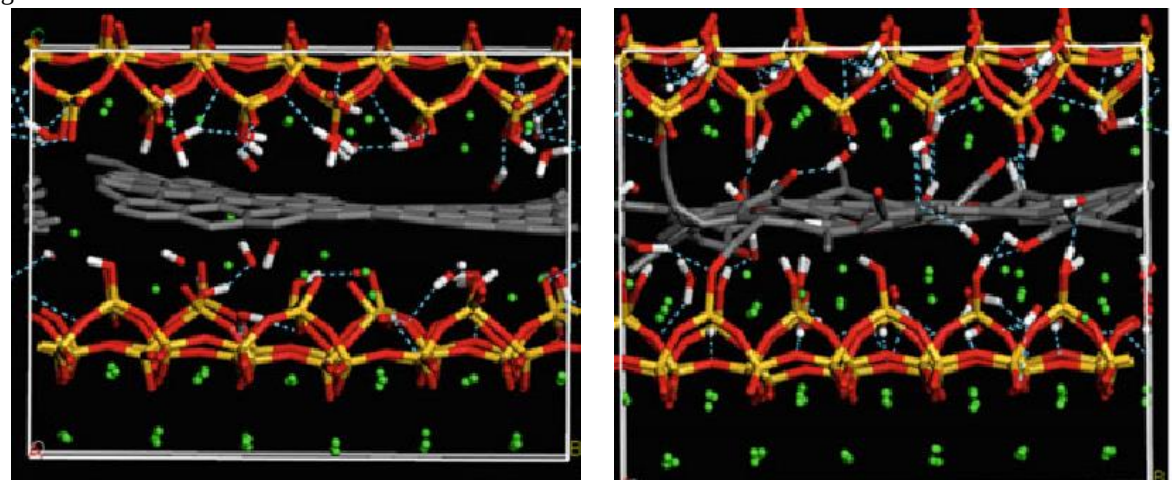
$N \approx 10^7$, characteristic of the mesolayer. The middle part of curve II in Fig. 2 was first described by Peris [22]:

$$\frac{dL(N)}{dt} = \acute{N}(\Delta E_{\acute{c}})^4, \quad (7)$$

where K is the stress intensity factor per cycle; C is the material constant. Both of these values should be determined experimentally.

Equation (4) shows: the number of cracks in concrete in the nanostructure region I is 10^5, in the mesoscopic region II is 10^7, and in the pre-destruction region III is about 10^9.

Since nanocracks always form when a surface layer is formed in a solid, it is possible to come up with a case of crack inhibition. This area includes modification of concrete by diluting cement with mineral nanopowders, among which, at present, graphene nanopowders are occupied [23]. In our work [24], we also obtained results on improving the properties of concrete (reducing nanocracks) with the addition of graphene obtained by liquid-phase exfoliation of graphite [25]. The structure of C–S–H obtained by molecular dynamics (MD) [15] with graphene (G) and graphene oxide (GO) is shown in Fig. 3.



a) *b)*

Figure 3. Structure of G/C–S–H and GO/ C–S–H [15]

It can be seen from Fig. 3 that graphene and graphene oxide are embedded in the interlayer space. Graphene and GO confined in the interlayer region of C–S–H gel exhibit different morphologies. In graphene, the carbon atoms ordered in the xy plane are distributed away from the C–S–H surface. No expansion along the z-direction is observed at the graphene/C–S–H interface in Fig. 3a. On the other hand, as shown in Fig. 3b, the protruding hydroxyls on both sides of GO indicate the C–S–H interface. The C–C bonds in GO are stretched in the z-direction, and the graphene sheet is damaged to some extent. Compared with standard concrete, the R(I) and R(II) values are halved and the elastic parameters of concrete are changed. The addition of graphene and graphene oxide to cement mortar significantly strengthens standard concrete (4-5 times) and reduces the amount of nanocracks.

Conclusion

The theory of cracks began to develop in the 20s of the last century and continues to develop to this day. A number of models of crack formation are presented in reviews [1-9]: the Griffiths model, Zener-Straw-Petch, Cottrell, Ballough-Gilman, Orvan-Straw, Koble, Nabarro-Herring and some others. However, none of the models presents the calculation of the crack length and its evolution. Our model shows that any body with a surface cannot be represented as an unlimited body - a technique known from classical mechanics. Cracks do not occur there. The difference in the interaction of near-surface atoms from the atom inside the solid leads to the occurrence of nanocracks, the evolution of which under certain conditions leads to the destruction of the solid. Our model, which is in development, allows us to determine the length of cracks in solids.

This scientific article was published as part of the grant funding for 2024-2026 IRN No. AP32488258 "Development of an innovative technology for obtaining graphene by intercalating graphite with microcluster water and modifying HTSC ceramics with graphene" (the study is funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan).

References:

1. Aruova L.B. Theoretical and practical aspects of combined solar thermal treatment of concrete in the conditions of dry hot climate of the Republic of Kazakhstan. - Diss. of Doctor of Technical Sciences, Moscow, 2006. - 242 p.

2. Mominova S.M. Development of technology for the production of gas silicate concrete based on phosphorus slags and polymineral sands in combination with natural wollastonite. - Diss. Doctor of Philosophy (PhD), Shymkent, 2021. - 155 p.

3. Elshibaev A.A. Study of low-temperature characteristics of asphalt concretes and polymer asphalt concretes. - Diss. Doctor of Philosophy (PhD), Almaty, 2022. - 121 p.

4. Ledenev V.V. Deformation and destruction of foundations, foundations, building materials and structures (theory, experiment): monograph - Tambov: Publishing center of FGBOU VO "TSTU", 2021. - 463 p.

5. Kuznetsov V.S. Reinforced concrete and stone structures. - M.: ASV Publishing House, 2022. - 360 p.

6. Lapshinov A.E. Strength and deformability of concrete columns reinforced with non-metallic composite reinforcement. - Diss. Cand. of Technical Sciences, Moscow, 2023. - 166 p.

7. Mehndi S.M., Khan M.A., Guide S.A. Causes and evaluation of cracks in concrete structures // International Journal of Technical Research and Applications, 2014, Vol. 2, Issue 5. - P. 29-33.

8. Hsu Th.T.C. (Editor). Concrete Structures in Earthquake. - Springer Nature Singapore, Pte Ltd, 2019. – 410 p.

9. Askar M.K., Al-Kamaki Y., Ferhadi R. and Majeed H.K. Cracks in concrete structures causes and treatments: a review // Journal of University of Duhok, 2023, Vol. 26, No.2. – P. 148-165,

10. Vettegren V.I., Ponomarev A.V., Kulik V.B. et al. Destruction of quartz diorite under friction // Geophysical research, 2020, Vol. 21, No. 4. – P. 35-50.

11. Vettegren V.I., Ponomarev A.V., Kulik V.B. et al. Nanocracks during oligoclase destruction // Physics of the Earth, 2021, No. 6. - P. 87-92.

12. Yurov V.M., Goncharenko V.I., Oleshko V.S. Study of primary nanocracks of atomically smooth metals // Letters to JTF, 2023, vol. 49, issue 8. - P. 35-38.

13. Yurov V.M., Goncharenko V.I., Oleshko V.S. Primary nanocracks in nitrides, borides and carbides of refractory metals // Physicochemical aspects of the study of clusters, nanostructures and nanomaterials, 2023, Issue 15. - P. 328-337.

14. Richardson I.G. The calcium silicate hydrates // Cement and Concrete Research, 2008, Vol. 38(2). – P. 137–158.

15. Hou D. Molecular Simulation on Cement-Based Materials. From Theory to Application. - Science Press and Springer Nature Singapore Pte Ltd. 2020. – 197 c.

16. Yurov V.M. Surface layer thickness of atomically smooth crystals // Physicochemical aspects of the study of clusters, nanostructures and nanomaterials. - 2019. - issue. 11. - P. 389-397.

17. Hamid S. The crystal structure of the 11 A natural tobermorite $Ca_{2.25}Si_3O_{7.5}(OH)_{1.5}\cdot H_2O$ // Zeitschrifit fur Kristallographie, 1981, Vol. 154. - P. 189–198

18. Allen A.J., Thomas J.J. and Jennings H.M. Composition and density of nanoscale calcium silicate hydrate in cement // Nature Material, 2007, Vol. 6. – P. 311–316.

19. Gleiter H. Nanostructured materials: basic concepts and microstructure // Acta mater., 2000, V. 48. - P. 1-29.

20. Yurov V.M., Ibatov M.K., Portnov V.S. On the issue of survivability of artillery gun barrels at the nanolevel // Bulletin of the National Defense University named after the First President of the Republic of Kazakhstan - Elbasy, 2022, No. 1 (93). - P. 135-140.

21. Poston T., Stewart I. Catastrophe Theory and Its Applications. Dover Publications, Incorporated, 2013. - 512 p.

22. Paris P.C., Erdogan F. A critical analysis of crack propagation laws // ASME J. Basic Eng., 1963, V. 85D. - P. 528-534.

23. Fayyad T.M., Abdalqader A.F., Sonebi M. An insight into graphene as an additive for the use in concrete // Civil Engineering Research in Irtland, 2022. – P. 67-72.

24. Zhangozin K.N., New method for obtaining graphene by intercalation of graphite with microcluster water. - Almaty: Darkhan, 2023. – 102 p.

25. Zhangozin K.N., Zhanabergenov T.K., Kargin D.B. About a new method for producing powder graphene // Bulletin of ENU named after. L. Gumileva, 2021, vol. 136, No. 3. – P. 8-16.