
PHYSICS OF SOLID STATE
AND CONDENSED MATTER

Studies of the Processes of Hardening of Cement Materials for the Storage of Aluminum Radioactive Waste by Neutron Radiography

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Abstract—The processes occurring during hardening of special cement pastes for the construction of storage facilities or disposal of radioactive waste containing aluminum metal were studied by means of a neutron radiography method. High reactivity of aluminum causes rapid release of hydrogen-containing components from the entire volume of cement paste. The cement pastes with organic additives to suppress the process of hydrogen-contained gases formation during the hardening of the cement materials were studied. Time dependences of the neutron attenuation coefficients for these special cement materials were obtained. Based on the neutron radiography data, the kinetics of hardening of those special cement pastes is discussed.

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INTRODUCTION

Cement-based materials are the key building components used in the construction of special-purpose facilities intended for the storage or disposal of radioactive waste of various types. Stringent criteria and requirements are imposed on such building materials in terms of their mechanical, physical, and chemical properties, as well as structural longevity of up to hundreds of years [1–3]. Special attention is paid to mechanical defects in cement and concrete structures such as cracks and cavities, which can cause the escape of radionuclides from the repository into the environment. Pores and cracks can be caused in cement materials not only by external factors, viz., humidity, temperature, etc., but also by the specific features of chemical reactions that occur during the hardening of the cement paste [4, 5]. The problem is especially acute as applied to cement materials intended for the long-term disposal or utilization of aluminum metal [4, 6, 7]. The reactivity of aluminum with the components of the cement paste results in the formation of a large number of cracks and hidden internal cavities, which motivates scientific research into the development of modified cement pastes with inorganic [8] or organic [5, 6] additives to suppress the mechanical degradation of the hardened cement or concrete [9, 10].

To bring cement-based materials promising from the point of view of storing radioactive waste in compliance with the technological requirements and the requirements for mechanical and chemical stability, numerous detailed studies into the structure of new cement materials and its validation are needed [9, 11]. Recently, a trend towards studying cement grades by nondestructive test methods has been visible [9, 12, 13]. One of these methods is neutron radiography [9, 11, 14]. The specific features and the nature of the interaction between neutrons and a substance determine the additional advantages of the method, such as the deep penetration of neutrons into the depth of massive objects, the sensitivity to the distribution of water and other aqueous compounds [14, 15] inside cement-based materials, and the noticeable radiographic contrast between the components containing light or heavy elements. Thus, the internal structure of several promising cement-based materials intended for the storage of aluminum radioactive waste has been studied by neutron tomography [9]. Based on the neutron data, spatial distributions of pores and cracks inside cement samples under investigation have been found using mathematical analytical algorithms. The results of this work underlay the recommendations for the optimization of production of particular cement matrices that can be used for the long-term storage of radioactive metal waste.

Table 1. Additives to the cement pastes, the hardening of which was studied in the experiment

Sample	Composition of cement paste
Cement_1	CEM V + 2.0H ₂ O
Cement_2	CEM V + 1.1H ₂ O
Cement_3	CEM V + 1.1H ₂ O + Al + Al ₂ (SO ₄) ₃ + C ₆ H ₈ O ₇ + PANTARHOL
Cement_4	CEM V + 1.1H ₂ O + Al + Al ₂ (SO ₄) ₃ + C ₆ H ₈ O ₇ + pantarhol + LiNO ₃

It should be noted, however, that the development of structural evolution models [1, 3] and the determination of temporal characteristic parameters of hardening of cement-based materials require radiographic experiments to study the kinetics of the cement paste hardening processed [16]. The results of such studies may be of great significance for optimizing the chemical synthesis of special-purpose cement grades. In this work, experiments were conducted to study the kinetics of the hardening of a cement paste based on Portland cement with various organic additives in the presence of aluminum metal using neutron radiography.

2. EXPERIMENTAL

The CEM V-A cement matrix, a detailed compositions of which was provided in previous works [8, 9], was chosen as the subject of the tests to study the kinetics of the hardening of cement-based materials designed for the storage of aluminum metal. For the experiments using neutron radiography, several cement-based materials with chemical additives were selected [5, 6]. The compositions of the resulting cement pastes are presented in Table 1. The **Cement_1** and **Cement_2** cement paste samples differ in the content of water added to cement powder. A large amount of water upsets the optimal ratio between the components of the cement paste, which may result in critical changes in the kinetics of the hardening processes.

The chemical components of the cement pastes were thoroughly agitated and placed into similar cylindrical alumina containers.

The neutron radiography images of the containers with the cement paste were obtained on a special-purpose experimental facility [17, 18] on the 14th channel of the IBR-2 high-flux pulsed reactor. The neutron images represent an array of data that characterize the degree or coefficient of neutron attenuation at a definite point of the sample under investigation [14]. The size of a pixel in the neutron radiography experiment was $54 \times 54 \mu\text{m}$. In the radiography experiment, neutrons were converted into visible light recorded by a CCD video camera by a 0.1-mm-thick RC TRITEC Ltd ⁶LiF/ZnS scintillator plate (Switzerland). The high neutron flux on the sample under examination determined the short exposure time of 10 s when recording a neutron image. The overall number of the neutron radiography images obtained in the experiment at an

imaging interval of 5 min was 72 and the total time of a neutron experiment to study the kinetics of hardening of the cement paste was 4.5 h, starting from the time when water was added to the cement powder. The correction for background interference of the detector system and the normalization to the incident neutron beam, as well as the visualization and analysis of the neutron radiography data, were performed using the ImageJ software package [19].

3. RESULTS AND DISCUSSION

Examples of characteristic neutron radiography images of the cement paste in an aluminum container for different time periods starting from the beginning of the experiment are shown in Fig. 1. The outline of the aluminum container is penetrable for the neutron beam, while the cement paste with a large amount of water greatly weakens the neutron beam [20].

During the first hour of the experiment, no changes were observed in the **Cement_1** cement paste with water excess. However, in the period from 1 to 3.5 h starting from the moment of adding water to cement powder, great changes were observed in the cement paste under investigation in the course of its hardening (Fig. 1a). The process was accompanied by the violent bubbling of the paste, predominantly from the area where the cement mixture contacted the walls of the aluminum container. In the course of time, the bubbling of the cement paste spread over the entire bulk of the material under investigation. Moreover, a cavity formed in the course of hardening between the bottom of the aluminum container and the cement paste was observed. During the third hour of the experiment, the volume of the cavity began to increase with time and, by the beginning of the fourth hour of the experiment, the volume of the cavity stopped increasing. The neutron radiography data make it possible to fairly accurately determine the volume of the cavity; 4 h after the beginning of the experiment, the height of the cavity reached 1.21(3) mm, which corresponded to a volume of 94.98(9) mm³. By that time, the bubbling and formation of cracks and cavities in the already hardened cement paste ceased (Fig. 1a).

The processes of cement paste bubbling during hardening can be caused by the release of water and/or hydrogen vapors [7, 21] as a consequence of hydration and hydrolysis reactions under the contact between

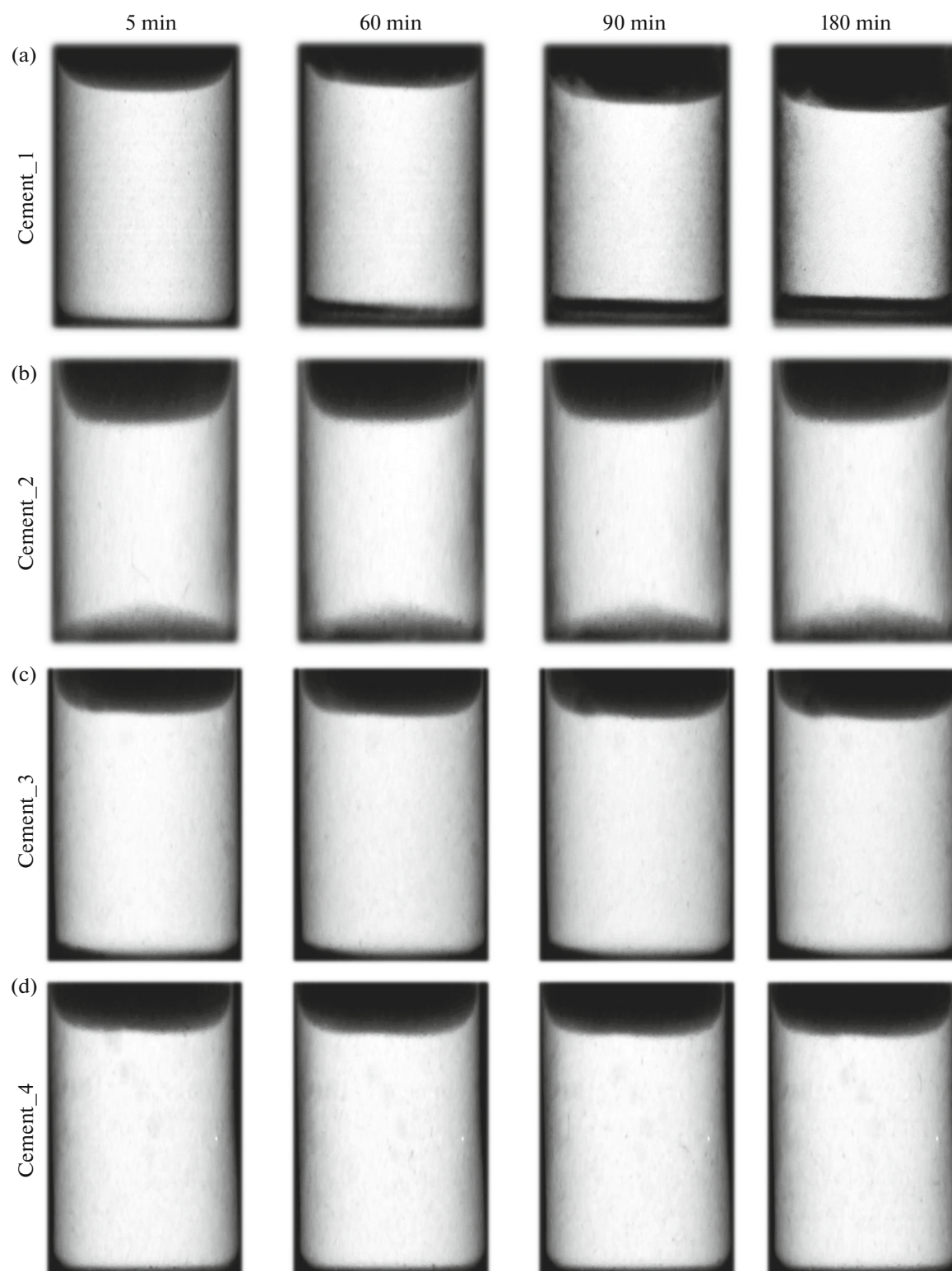


Fig. 1. Neutron radiography images of the cement pastes under investigation obtained at different time points during the hardening of the pastes. The light areas in the neutron images correspond to the high degree of the neutron attenuation inside the cement paste. The walls of the aluminum container are penetrable for neutrons when compared with the cement paste.

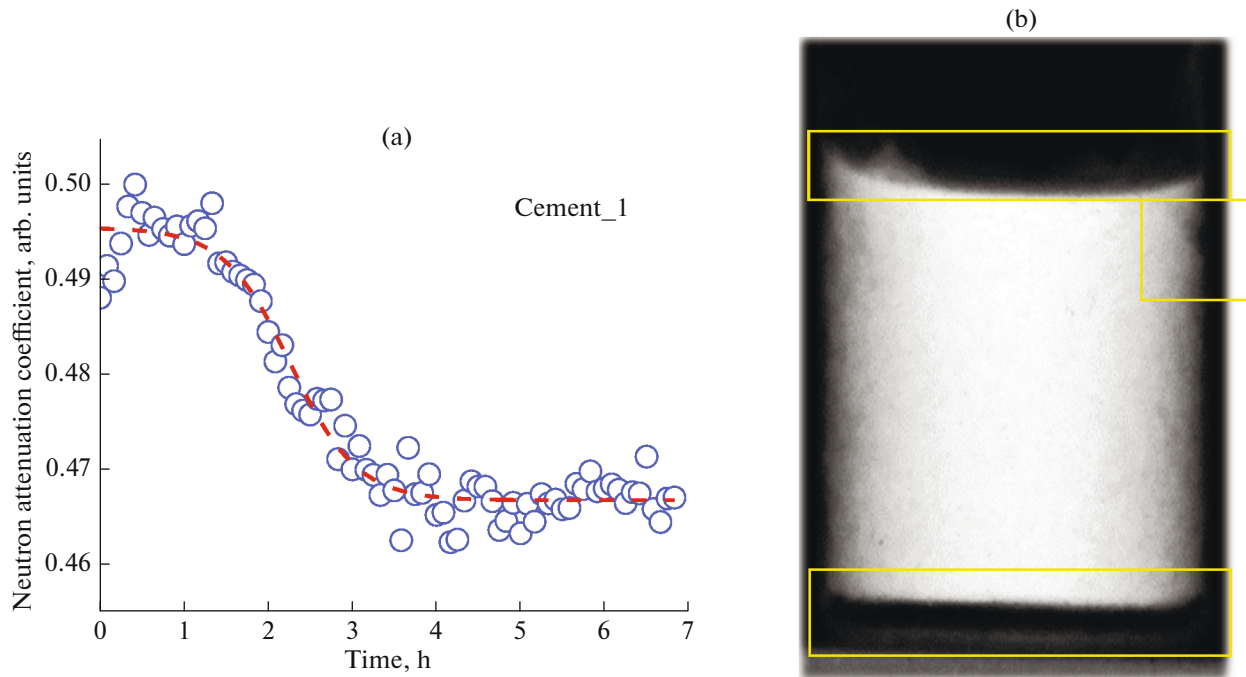


Fig. 2. (a) Dependence of the neutron attenuation coefficient on the hardening time of the **Cement_1** paste. The dashed line denotes the interpolation of the experimental data by the Boltzmann function [27]. (b) Radiography image of the hardened cement paste with marked inhomogeneities induced by the hardening process, viz., surface roughness, a crack between the wall of the aluminum container and the cement material, and a cavity at the bottom of the container.

the cement paste and the aluminum container and the exchange interaction that occurs during the mixing of cement with water in the liquid phase or on the surface of solid cement particles [22]. Such chemical reactions may be accompanied by the contraction effect [21, 22], characterized by a reduction in the absolute volume of the cement–water system when compared with the volumes of the source components. This effect may be the cause of the formation of the cavity at the bottom of the container (Fig. 1a). To support the assumption about the release of hydrogen or water vapors out of the cement paste, the neutron attenuation coefficient Σ_{cem} was calculated [20] for different hardening times. The time dependence of the coefficient for the **Cement_1** paste is shown in Fig. 2. In the dependence, three characteristic time periods can be clearly seen. The first time interval from 0 to 1.2 h is characterized by a practically constant neutron attenuation coefficient and is probably related to the interaction of neutrons with the cement paste and insignificant effects resulting from the evaporation of water. A slow lime hydration reaction may also occur at that time [23]; the concentration of the calcium hydroxide formed is, however, insufficient for the continuation of the chemical reactions with other cement paste components. During the second time interval, 1.2–3.8 h, a noticeable decrease in the neutron attenuation coefficient in the cement paste is observed (see Fig. 2a). This time interval corresponds to the beginning of the release of excessive hydrogen and water vapors in the

course of dissociation of carbonates out of the entire bulk of the cement paste [22]. After 4 h of the experiment, the neutron attenuation coefficient almost does not change, which may correspond to the termination of the chemical reactions in the cement-based material under investigation in which reactions water and hydrates participate or to a considerable reduction in the intensity of the above reactions. During this period, the hydration and chemical binding of water continue; the plasticity of the cement paste decreases and it noticeably thickens; and the setting and hardening occur, after which the cement starts to acquire strength. However, the chemical reactions in the hardened cement may last for several years [24].

The pattern of changes in the neutron attenuation coefficient can indicate the first approximation the applicability of the formalism of the phase transition kinetics [25, 26], in which definite stages are singled out, viz., the formation of a new phase of the compound in the original phase, i.e., the nucleation process, the growth in the volume of the new phase, and the corresponding disappearance of the original component. In this case, the cement hardening kinetics can be described by an exponential function of time as [25]

$$X(t) = 1 - \exp(-kt)^n, \quad (1)$$

where X is the volume fraction of the new phase; t is the time; $k \sim 1/\tau$ is a function that expresses the dependence of the phase transition rate on the temperature, pressure, grain size, or internal stresses; τ is

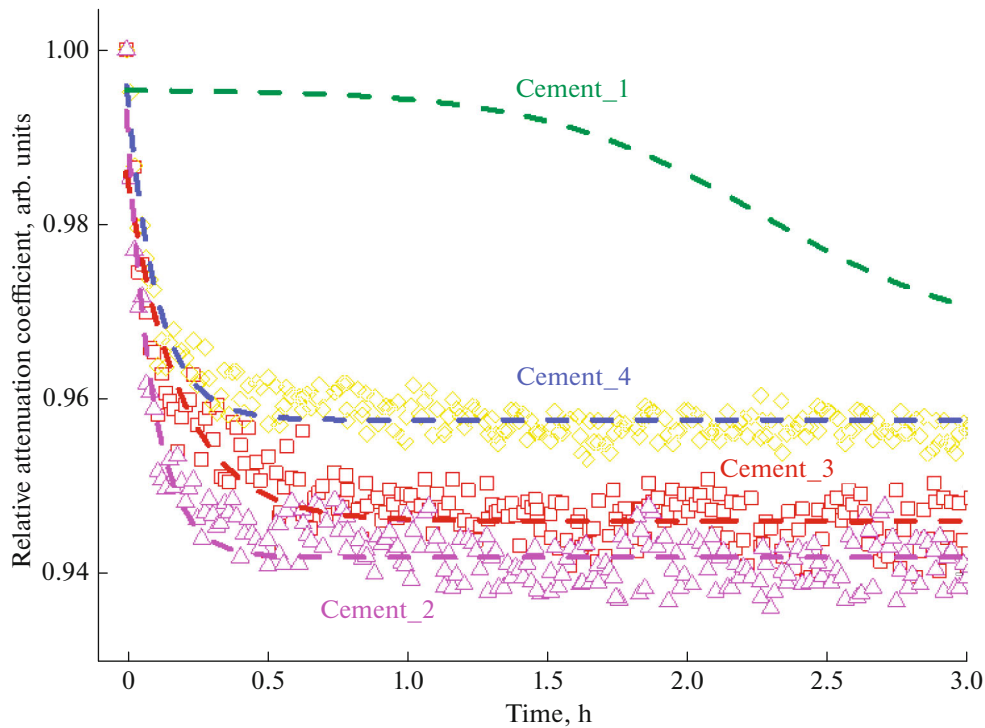


Fig. 3. Dependence of the neutron attenuation coefficient on the hardening time of the **Cement_2**, **Cement_3**, and **Cement_4** materials. The dashed line denotes the interpolation of the experimental data by the Boltzmann function [27].

the lifetime of the mixed phase state; and n is a parameter that characterizes the transient processes of the phase transition, viz., the rate and probability of the nucleation of a new phase, the growth rate, etc. Then, based on the neutron radiography data, the “lifetime” τ [25] of the hardening phase of the cement paste can be assessed as $\tau \sim 132$ min. It should be noted that the calculation is a strictly rough estimation, since the chemical processes that occur in the cement paste during its hardening are of a more complicated nature.

The addition of organic components to the cement paste results in the suppression of the processes of gas release and binding of hydrogen-containing components [2]. In Figs. 1b–1d, neutron radiographic images of the containers with the **Cement_2**, **Cement_3**, and **Cement_4** pastes are shown. During the four hours of the experiment, the release of the gas accompanied by weak bubbling was observed only in the **Cement_2** sample without any additives. In the neutron radiography images of the cement pastes with additives, no changes with time were observed. The radiography experiment yielded neutron attenuation coefficients Σ_0 for the cement pastes under investigation at the initial point of time of the experiment. They were 0.53(2), 0.64(3), and 0.68(4) for the **Cement_2**, **Cement_3**, and **Cement_4** samples, respectively. The time dependences of the relative attenuation coefficient Σ/Σ_0 , where Σ_0 is the respective initial value, are shown in Fig. 3. It can be seen that, for the **Cement_2**, **Cement_3**, and **Cement_4** samples, no intermediate area of the violent release of hydrogen and/or water

vapors characteristic of the **Cement_1** sample (see Fig. 2a) are observed. However, during the first 20 min of the experiment, a drastic reduction in the neutron attenuation coefficient is observed, which may be related to the simple evaporation of water from the surface of the cement paste or through the pores in the material [22, 23]. As the experiment proceeds, no noticeable changes in the time dependences of the neutron attenuation coefficients of these three cement-based materials are observed.

It should be noted, however, that, in the **Cement_2** compound without any additives, the dehydration process occurs somewhat faster: during the first half an hour, the change with time in the neutron attenuation coefficient is $d\Sigma/dt = 1.3(2) \text{ h}^{-1}$, while the rate of change in the coefficients of the neutron transmission of the **Cement_3** and **Cement_4** pastes was $d\Sigma/dt = 0.9(2) \text{ h}^{-1}$. This may imply the chemical binding [23] of the hydrogen-containing components inside the **Cement_3** and **Cement_4** pastes, which reduces the probability of formation of cracks and cavities inside the hardened cement [8, 9]. At 3.5 h of the experiment, high neutron attenuation coefficients, 0.61(2) and 0.65(2), are characteristic of the **Cement_3** and **Cement_4** pastes, respectively. This also implies the binding of the hydrogen-containing components inside the cement pastes. Therefore, the **Cement_3** and **Cement_4** materials with organic additives, which chemically suppress the violent release of hydrogen-containing components during the hardening of the

cement pastes when in contact with aluminum or its compounds, can be considered to be potential candidates for the materials used to construct radioactive waste repositories [2, 3].

4. CONCLUSIONS

The processes that occur during the hardening of cement pastes in the presence of aluminum have been studied by neutron radiography. The high reactivity of aluminum causes a violent release of hydrogen-containing components from the entire bulk of the cement paste. As a result, internal cavities and cracks are formed in the hardened cement. The addition of organic components to the cement paste leads to the retardation and suppression of the above processes, which offers great possibilities for using cement samples of this kind as materials for construction of facilities for storage or disposal of radioactive waste that contains aluminum metal.

REFERENCES

1. Y. Amano, G. Bruno, A. Bychkov, and E. Cody, "Radioactive waste: meeting the challenge," *Sci. Technol. Safe Sustainable Solut.* **41**, 45 (2014).
2. F. Dragolici, M. Bucataru-Nicu, L. Lungu, C. N. Turcanu, and Gh. Rotarescu, "Durability of cemented waste in repository and under simulated conditions," *IAEA-TECDOC-1397* (2004), Vol. 21, p. 137.
3. J. R. Helliwell, "Radioactive waste limits in cement to avoid leaching out," *J. Appl. Crystallogr.* **47**, 4–5 (2014).
4. A. I. Onuchukwu, "Corrosion inhibition of aluminium in alkaline medium. I: Influence of hard bases," *Mater. Chem. Phys.* **20**, 323 (1988).
5. M. Nicu, L. Ionascu, C. Turcanu, and F. Dragolici, "Use of lithium nitrate as a potentially corrosion inhibitor for radioactive aluminium in cementing systems," *Rom. J. Phys.* **60**, 1193–1202 (2015).
6. M. Nicu, L. Ionascu, C. Turcanu, F. Dragolici, and Gh. Rotarescu, "Study of the conditioning matrices for aluminium radioactive wastes," *Rom. J. Phys.* **59**, 360–368 (2014).
7. T. Matsuo, T. Nishi, and M. Matsuda, "Prevention of hydrogen gas generation from cement solidified aluminium wastes," *Trans. Am. Nucl. Soc.* **72**, 76 (1995).
8. L. Ionascu, M. Nicu, C. Turcanu, F. Dragolici, and Gh. Rotarescu, "Chemical composition of radioactive waste and the mechanical performance of cemented matrix," *Rom. Rep. Phys.* **65**, 1512–1518 (2013).
9. S. E. Kichanov, K. M. Nazarov, D. P. Kozlenko, M. Balasoïu, M. Nicu, L. Ionascu, A. C. Dragolici, F. Dragolici, and B. N. Savenko, "The neutron tomography studies of the cement materials used for radioactive waste storages," *Rom. J. Phys.* **64**, 12 (2019).
10. Yan-Shuai Wang and Jian-Guo Dai, "X-ray computed tomography for pore-related characterization and simulation of cement mortar matrix," *NDT & E Int.* **86**, 28–35 (2017).
11. H. Justnes, K. Bryhn-Ingebrigtsen, and G. O. Rosvold, "Neutron radiography: an excellent method of measuring water penetration and moisture distribution in cementitious materials," *Adv. Cem. Res.* **6** (22), 67–72 (1994).
12. P. Zhang, F. H. Wittmann, P. Lura, H. S. Muller, S. Han, and T. Zhao, "Application of neutron imaging to investigate fundamental aspects of durability of cement based materials: review," *Cem. Concr. Res.* **108**, 152–166 (2018).
13. U. M. Angst, R. D. Hooton, J. Marchand, C. L. Page, R. J. Flatt, B. Elsener, C. Gehlen, and J. Gulikers, "Challenges and opportunities in corrosion of steel in concrete," *Mater. Struct.* **63**, 1047–1051 (2012).
14. I. S. Anderson, R. L. McGreevy, and H. Z. Bilheux, *Neutron Imaging and Applications: A Reference for the Imaging Community* (Springer, New York, 2009), p. 241.
15. E. H. Lehmann, A. Kaestner, C. Gruenzweig, D. Mannes, P. Vontobel, and S. Peetermans, "The effect of water repellent surface impregnation durability of cement-based materials," *Int. J. Mater. Res.* **105**, 664–670 (2014).
16. C. Hall, "Water sorptivity of mortars and concretes: a review," *Mag. Concr. Res.* **41** (147), 51–61 (1989).
17. D. P. Kozlenko, S. E. Kichanov, E. V. Lukin, A. V. Rutkauskas, G. D. Bokuchava, B. N. Savenko, A. V. Pakhnevich, A. Yu. Rozanov, "Neutron radiography facility at IBR-2 high flux pulsed reactor: first results," *Phys. Proc.* **69**, 87–91 (2015).
18. D. P. Kozlenko, S. E. Kichanov, E. V. Lukin, A. V. Rutkauskas, A. V. Belushkin, G. D. Bokuchava, and B. N. Savenko, "Neutron radiography and tomography facility at IBR-2 reactor," *Phys. Part. Nucl. Lett.* **13**, 346–351 (2016).
19. C. A. Schneider, W. S. Rasband, and K. W. Eliceiri, "NIH image to ImageJ: 25 years of image analysis," *Nat. Meth.* **9**, 671–675 (2012).
20. V. F. Searf, "Neutron scattering lengths and cross sections," *Neutron News* **3**, 29–37 (1992).
21. A. I. Onuchukwu, "Corrosion inhibition of aluminium in alkaline medium. I: Influence of hard bases," *Mater. Chem. Phys.* **20**, 323 (1988).
22. R. Berliner, M. Popovici, K. W. Herwig, M. Berliner, H. M. Jennings, and J. J. Thomas, "Quasielastic neutron scattering study of the effect of water-to-cement ratio on the hydration kinetics of tricalcium silicate," *Cem. Concr. Res.* **28**, 231–243 (1998).
23. R. Kondo and Sh. Kondo, "Kinetics and mechanism of cement hydration," in *Proceedings of the 5th International Congress on Cement Chemistry* (Stroiizdat, Moscow, 1973), pp. 185–204.
24. T. A. Lychagina, D. I. Nikolayev, M. Balasoïu, M. Nicu, L. Ionascu, A. C. Dragolici, and F. Dragolici, "Aging studies of low pH cement-based materials used for aluminium radioactive waste conditioning," *Rom. J. Phys.* **64** (802), 12 (2019).
25. M. Avrami, "Kinetics of phase change. III. Granulation, phase change, and microstructure," *J. Chem. Phys.* **9**, 177–184 (1941).
26. L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics, Vol. 5: Statistical Physics* (Nauka, Moscow, 1995; Pergamon, Oxford, 1980), p. 28.
27. L. Gold, "Statistical theory of phase change," *J. Chem. Phys.* **29**, 51 (1957).

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