Final Research Report on grant NN 127102: V4 Korea RADCON - The Effect of Chemical Composition of Concrete on Its Long-term Performance in Irradiated Environment

Introduction

The chemical composition of concrete constituents is a key factor influencing the ageing of the NPPs, thus structural integrity (durability and service-lifetime), as well as the activation and radiation shielding properties of concrete structures. The sustained operation and future decommissioning of the Paks nuclear power plant (NPP) and the deployment of new Paks II blocks make this study timely and economically relevant. To comply with the ALARA principle of nuclear engineering, all raw materials (to be) used in nuclear applications need to be characterized. In a neutron field, such as the biological shielding near the reactor pressure vessel, or structures at neutron research facilities, raw materials with low levels of impurities (e.g. Co, Eu, precursor elements of activation products) must be selected to minimize persistent radioactivation. By systematic analytical work and material testing procedures beyond the industrial standards, we screened a broad range of domestic mine products (gravel, sand) and cement, and considered these aspects specific to nuclear applications. The Centre for Energy Research (EK), as the Hungarian partner in the V4-Korea RADCON collaboration, covered a wide range of experimental investigations: composition analysis of raw materials, identifying the suitable low-activation types based on their chemical composition, test irradiations and activation measurements of bulky specimens, and numerical modeling of radioactivation verified on these experimental data.

Sample collection

Classifying the various domestic gravel pits based on the variabilities of their trace-element contents was a key task in the project: it brought new geological knowledge with technological relevance and is important in concrete production technology for NPP [1]. As previous data were very scarce and divergent, we needed a solid basis of compositional data for the development of models and the final assessment. Adequate concrete constituents (gravel, sand, cement) were identified and collected with a focus on domestic raw material sources.

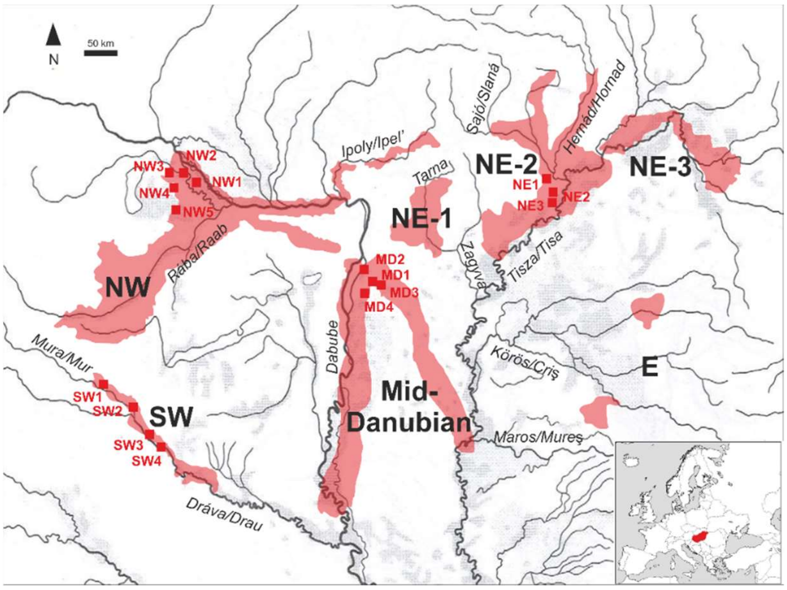


Figure 1: Domestic sampling localities of this project with major pebble mining regions.

Our sampling included four major depositional regions (NW, Mid-Danubian, SW, and NE-Hungarian Region) with 16 localities (***Figure 1***) and four grain-size fractions each (involving gravel and sand samples). Products of domestic cement suppliers (DDC Beremend and Vác) were represented with 36 items containing different types of binders. In addition, 39 domestic aggregates (hematite, barite, magnetite, basalt, andesite, limestone) and 16 clinker and clay samples were measured. We also analyzed samples supplied by our project partners (SK: 18 aggregate and cement, CZ: 5 aggregate, PL: 22 aggregate and cement, KR: 7 aggregate) and compared them with the

Address: 29-33 Konkoly-Thege Miklós street, H-1121 Budapest, Hungary
Mailing address: P.O.B.: 49, Budapest, H-1525.
E-mail: szentmiklosi.laszlo@ek-cer.hu
Phone.: +36 1 392 2539
Web: www.ek-cer.hu

corresponding Hungarian mine products. Further, several additives (clay, limestone, slag, ore powder, ore slag, gypsum, and clinker) and admixtures were also analyzed for their impurities.

Sample composition characterization, analytical methodology

Before starting the large-scale analytical study, the detector calibration procedure of NAA was improved to achieve more correct results for elements determined via their high-energy gamma emitter radionuclides [2]. We took advantage of the correction methods developed in a parallel OTKA research K124068 for large-sample PGAA [3]. We procured a Retsch Jaw Crusher BB 50, that in combination with our Retsch MM200 mixer mill, was extensively used for the crushing and powdering of the collected gravel samples.

The chemical characterization of the samples by the newly established NEAAA (neutron-based elemental analysis and activation assessment) protocol involved prompt gamma activation analysis (PGAA) and instrumental neutron activation analysis (NAA) measurements performed at the Budapest Research Reactor, and in some cases supplemented by X-ray fluorescence (XRF) measurements. This complex analytical procedure was necessary to cover a much wider range of elements than usual, concerning both the neutron-induced radioisotopes (Ce, Co, Cs, Eu, Fe, Hf, Sb, Sc, Ta, Tb, Cr, Pa, Sm, Sr, Zn, Th, and U) responsible for medium- to long-term activities, and the relevant contaminations generated during the processing (e.g. crushing, mixing) the raw materials. For the systematic storing of the results, an Excel-based database was established.

Petrographic characterization

As a complementary geochemical categorization of the domestic sand and gravel samples, petrographic (macroscopic, microscopic, and heavy mineral) investigations were made on gravels from all four regions [4]. Macro- and micro-scale gravel petrography of the samples proved diagnostic differences and the concentration of neutron-induced radioisotopes responsible for medium- to long-term activities in the so-called heavy minerals of the sand and gravel, which affects their activation properties. The results made up a comprehensive dataset that provided input to the following step of the research, the evaluation of activation potential.

Heavy mineral study of sand samples from the previously examined NW Hungarian localities was also made in the framework of a BSc thesis [5], to highlight the mineralogical sources of long-lived radionuclide content. Mineralogical (by stereomicroscopy) and chemical composition (by NEAA) could be correlated and exact mineral phases could be determined as carriers of the relevant radionuclides. A PGAA beam time proposal at FRM II reactor, in Garching, Germany has been submitted to analyze the tiny separata that are too small to be measured using our setup.

Elemental Composition Results

Analytical and geochemical studies of the domestic gravels [1] led to the conclusion that all regions show similar major and trace element patterns but with regional differences (e.g. Ca vs. Mg content, average trace element content). Elemental analysis of the samples rated by particle size revealed that all the element concentrations decrease with increasing particle size, except for Cr, which has a higher concentration in gravels than in sands. Grinding the samples with tungsten carbide mortar resulted in detectable levels of W, Ta, and also significant Co impurities in the samples. The contamination issue of this technique has to be considered when planning technological procedures at an industrial scale. Mg, Ca, and Sr enrichment and their large variability are due to the abundant but varied carbonatic sedimentary rock content (e.g in the NW Region). Enriched Ti, Al, Na, K contents refer to the presence of clay minerals (e.g in the SW Region). The

Address: 29-33 Konkoly-Thege Miklós street, H-1121 Budapest, Hungary
Mailing address: P.O.B.: 49, Budapest, H-1525.
E-mail: szentmiklosi.laszlo@ek-cer.hu
Phone.: +36 1 392 2539
Web: www.ek-cer.hu

mine of Babót (NW Region) has the most mature sediment formation, also indicated by high Si content at the expense of depleted other major and trace elements. We concluded that, fortunately, none of the long-lived radionuclide precursor elements are enriched significantly in the investigated sand and gravel samples compared to the average Portland cement composition (***Figure 2***).

Fe (0.5-1.5 m%) and Cr, Sr (a few hundred µg/g) show slightly higher concentrations, but all have half-lives of less than a year. Cs, Co, and Eu, with years-long half-lives, are under 5 µg/g concentration in gravels. It is a technological conclusion from our results that it is better to use crushed material of larger gravel fractions than sand to prepare low activation susceptibility shielding concrete. Volcanic rocks (basalt and andesite) as extra aggregates are not recommended for use in shielding concrete, as their Cs, Co, and Eu content is far higher than in average Portland cement, or in other cement types (CEM II, III, IV, V).

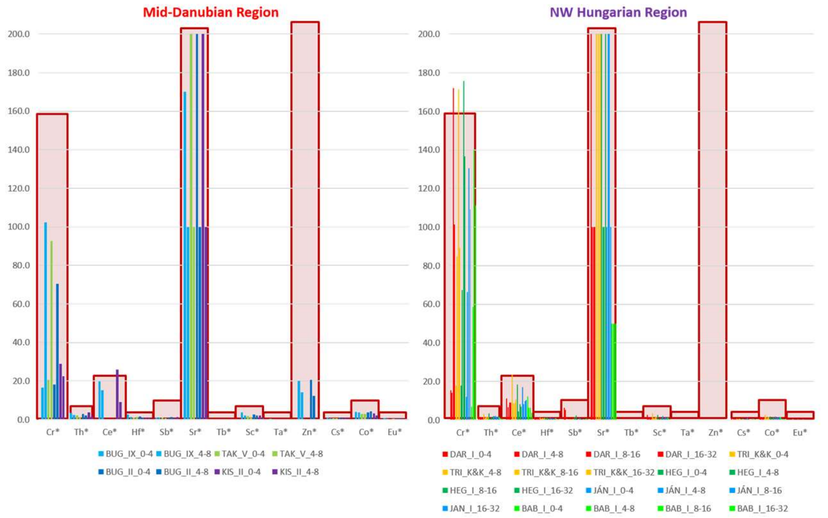


Figure 2: Concentrations of long-lived isotopes in gravels from the Mid-Danubian and NW Hungarian Regions. Red bars indicate the trace element compositions of average CEM-I Portland cement. [6]

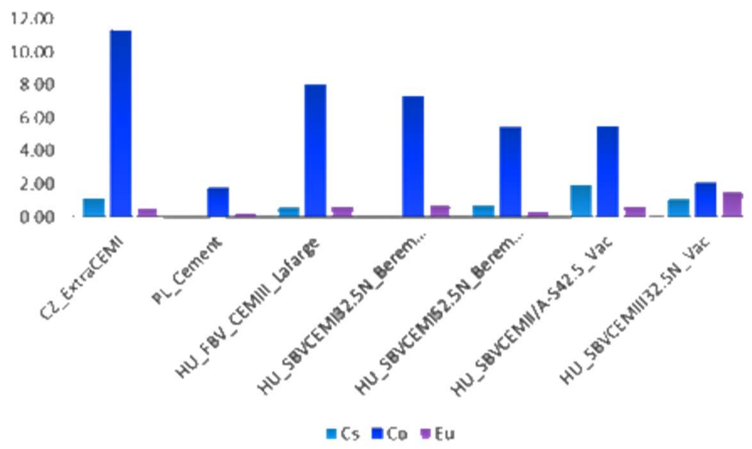
We provided compositional data for constituents of heavy-weight concrete (with high-density aggregates, barite, and magnetite) designed by the Slovakian partners [7,8]. Experiments were completed on blended cement with supplementary cementitious materials (blast furnace slag, metakaolin, silica fume/limestone) to optimize the hydration heat (determined by conduction calorimetry). The results showed that aggregate content and not the binder is the main factor influencing the engineering properties (thermal conductivity, volumetric specific heat, thermal diffusivity, volume expansion, shrinkage) of heavy-weight concretes.

Further chemical investigations of foreign aggregate, cement, and admixture samples and their correlation with domestic aggregate and cement focused on the assessment of the fine aggregate suitability for concrete affecting the long-term durability in relation to alkali-silica reaction (ASR) [9]. Our proposed procedures to determine the ASR risk of aggregate shed light on the strong correlation between sand origin and its susceptibility to ASR. Our chemical characterization data also provided a basis for recommendations on the disposal of cement-based composites as radioactive waste after the decommissioning of nuclear power plants [10]. The use of material with low-activation constituents could effectively reduce the radioactivity of concrete. Decommissioning costs can decrease due to reducing radioactive concrete waste.

Via elemental composition measurements of domestic and foreign concrete constituting materials, we identified low-activation gravel-, sand-, and cement types (***Figures 3, 4***), recommended for concrete used in a high-radiation environment [11,4,1]. Appropriate candidates for aggregates in heavy-weight concrete and low-activation blended cement were selected and tested [12]. Products of Hungarian mines and domestic suppliers (sand, gravel, additives, and binders), candidates for use in hydrate and heavy concrete, are proven to be equally adequate in shielding concrete production concerning their activation potential [1,4]. Some of

Address: 29-33 Konkoly-Thege Miklós street, H-1121 Budapest, Hungary
Mailing address: P.O.B.: 49, Budapest, H-1525.
E-mail: szentmiklosi.laszlo@ek-cer.hu
Phone.: +36 1 392 2539
Web: www.ek-cer.hu

the analyzed gravels and magnetite have relatively high cobalt contents, which must be considered when applying them as shielding-concrete constituents.



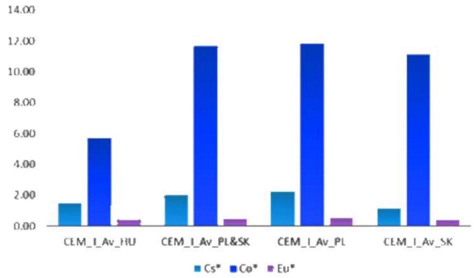


Figure 3: (left) Concentrations of long-lived isotopes in Hungarian cement types and (right) average concentrations of long-lived isotopes in Hungarian, Slovakian, and Polish CEM-I cement samples.

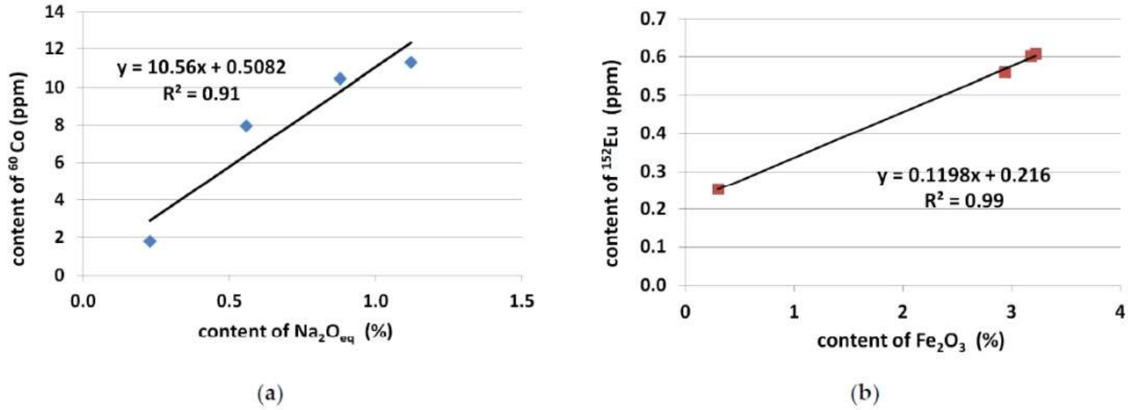


Figure 4: Concentration of long-lived isotopes in Portland cements depending on (a) the alkali content and (b) the iron content.

Test irradiations of concrete specimens

Test mortar specimens prepared by our Polish partners were irradiated. Therefore, neutron flux was characterized and the irradiation conditions were optimized. A set of 20×20×80 mm concrete bars was irradiated in the BRR for 24 hours. The temperature has been monitored during activation with heat stamps. Currently, the test specimens are still very active and difficult to handle and measure safely, even in a well-equipped radiochemistry laboratory.

In parallel, based on the collected nuclear analytical data of raw materials we started to predict the neutron-induced sample activity by calculations. Neutron fluxes inside the vertical irradiation channels of the Budapest Research Reactor (BRR), where the parallel irradiations of the concrete blocks were performed, have been characterized by irradiating a set of metal foils. The analytical calculation procedure of the detailed flux measurements and related Monte Carlo calculations were worked out (***Figure 5***). Comparison of the

Address: 29-33 Konkoly-Thege Miklós street, H-1121 Budapest, Hungary
Mailing address: P.O.B.: 49, Budapest, H-1525. **Phone.**: +36 1 392 2539
E-mail: szentmiklosi.laszlo@ek-cer.hu **Web**: www.ek-cer.hu

results on concrete test specimens and the FISPACT modeling paved the way to predict activation without further irradiations, saving efforts, radioactive waste, and costs and conclude about not-yet-built designs [13].

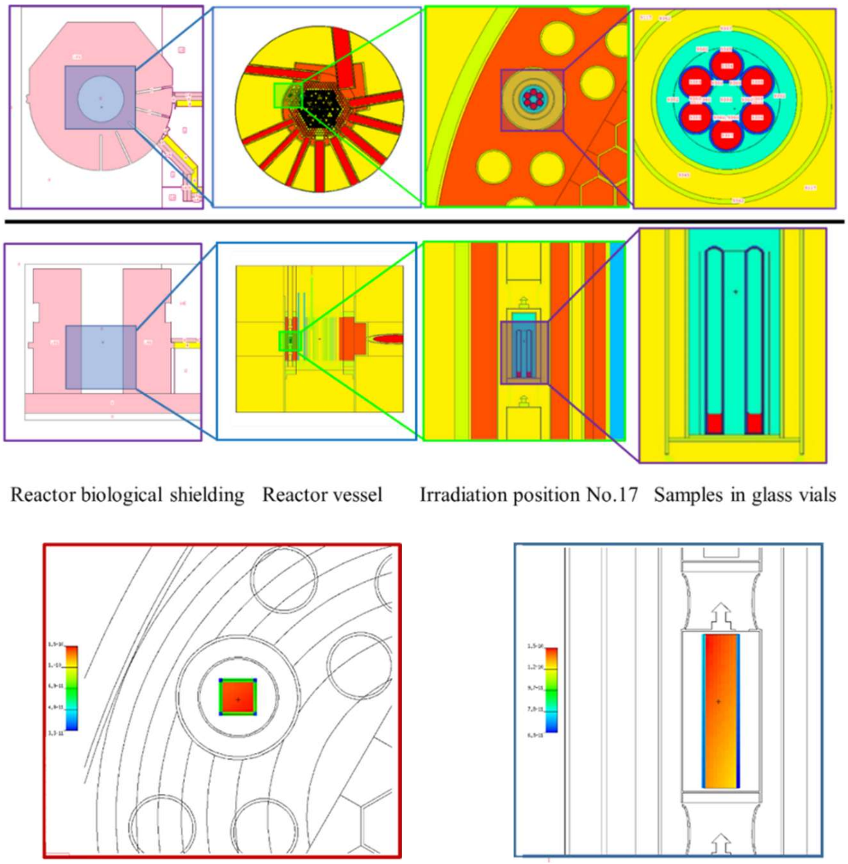


Figure 5: (top) Irradiation position in the full-scale MCNP6 model of the BRR. (bottom) Upscaling the activation of a point-like sample to a case of a bulky concrete bar.

Activation assessment and method validation

To predict and plan the activities of samples, an MCNP reactor core model was built and was used for simulations. We predicted inventories of radioisotopes produced by neutron exposure of realistic materials (measured composition data from PGAA and NAA) in the BRR in the specific irradiation geometry of the No. 17 channel. The energy- and spatial distributions of the neutron field calculated by the full-scale MCNP6 model were transferred to FISPACT, and the resulting activities were validated against those measured using neutron-irradiated small samples and upscaled to bulky targets.

The activities from the calculations were compatible with the experimentally measured activities derived from the irradiations in the BRR. This validated approach is general enough to handle different target materials, shapes, and irradiation conditions [13,14].

Following this benchmarking, the method was applied to predict the activation properties of the near-vessel concrete of existing NPPs (e.g. BRR) or assist in the optimal construction of new NPP units (e.g. Paks II). In addition to the major contributors of gamma dose rate in concretes, the calculation also accounts for the decays without gamma emissions, i.e. invisible to our irradiation experiments.

Address: 29-33 Konkoly-Thege Miklós street, H-1121 Budapest, Hungary
Mailing address: P.O.B.: 49, Budapest, H-1525.
E-mail: szentmiklosi.laszlo@ek-cer.hu
Phone.: +36 1 392 2539
Web: www.ek-cer.hu

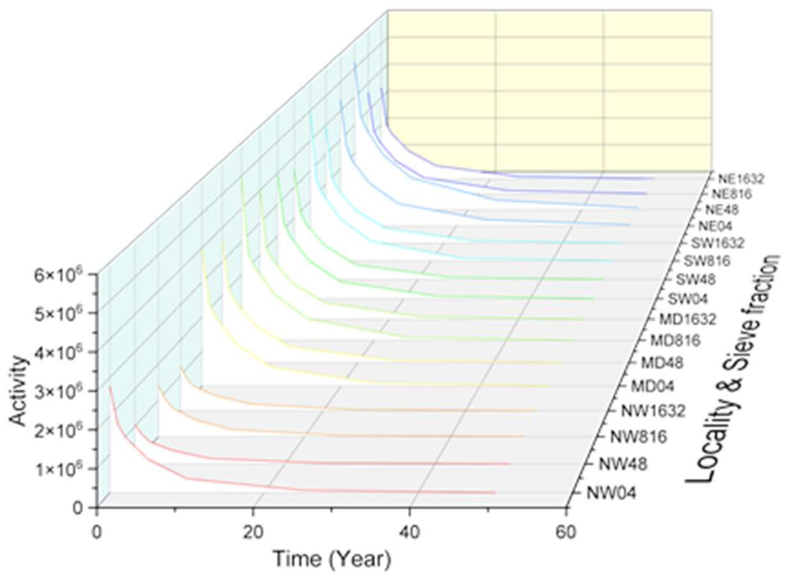


Figure 6: The activity profile of fictitious near-vessel shielding concrete made of gravel and sand products of different localities.

We concluded that near-vessel concrete made of different mine products may show activity differences up to a factor of 4, but all decay completely within 30 years (***Figure 6***) [1].

In 2022, based on the know-how of the project, calculations supporting the new shielding bunker design for the RAD station of the BRR were done [15]. The horizontal neutron beam was characterized by activation foil measurements and MCNP core simulation. The composition, thickness, and density of the layered structure made of concrete and a boron-containing neutron shielding layer were optimized. Detailed dose-rate maps were calculated to visualize the attenuation capability of the shielding and to reveal the weak points of the structure. The optimized shielding bunker is being realized soon.

Solid mechanics

Together with our Czech project partners, the mechanical response of the concrete ring around a reactor pressure vessel to prolonged exposure to neutron irradiation was modeled [16], considering the damage generated by neutron radiation in the analysis.

Neutron radiography studies were designed for the detailed characterization of the formation and aging processes of concrete. Integrated neutron-based studies, i.e. combination of chemical and structural information and methods were successful by-products of our project. These activities involved increasing experimental work at our imaging facilities (NIPS-NORMA and RAD).

The degradation of shielding concretes of NPPs was studied by dynamic thermal-neutron radiography of experimental gamma-irradiated early-age hardened cement samples in the framework of a Ph.D. research hosted by our Czech collaborator [17-19]. Structural damage was observed through water uptake during imbibition correlating with the nano-microscale porosity and absorption capability of the matter.

The radiation-induced volumetric expansion (RIVE) and the thermal expansion of concrete were numerically modeled [20] for the concrete biological shield of VVER-440/213 reactors. According to the results, the damage to the concrete biological shield will not affect the load-bearing function of the containment building of the reactors. Though the shielding properties of the biological shield may be reduced due to the appearance of the radial cracks, the external concrete wall might still ensure the necessary shielding.

The most impactful publication came as a result of an unforeseen field of collaboration, where X-ray and neutron tomography (XCT and NCT), and optical microscopy (OM) techniques were combined to characterize the pore system of concrete. Numerical parameters (i.e. spacing factor to quantify the void-to-void proximity) were determined by the three independent methods owing to different 2D or 3D resolutions.

Address: 29-33 Konkoly-Thege Miklós street, H-1121 Budapest, Hungary
Mailing address: P.O.B.: 49, Budapest, H-1525. **E-mail:** szentmiklosi.laszlo@ek-cer.hu
Phone.: +36 1 392 2539 **Web**: www.ek-cer.hu

The experiments provided good agreement between the OM and XCT both for the calculated spacing factor (L) and the total porosity (A). The combined NCT/XCT dataset offered the best discrimination between the concrete constituents (***Figure** 7*). The segmented microstructure was fed to a beyond-state-of-the-art finite element calculation that relied on the real microstructure of the sample. Detailed and accurate stress and strain fields of the material were obtained (***Figure 8 a)***) [21]. A further methodological comparison of void-to-void proximity calculations using neutron and X-ray tomography is in progress [22].

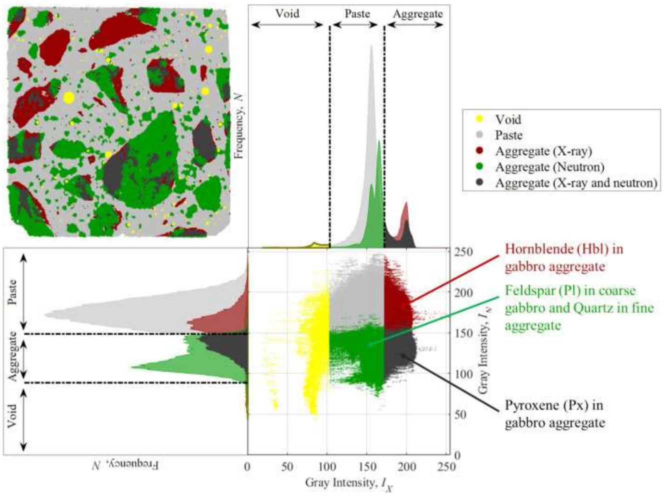


Figure 7: Bimodal (X-ray and neutron-based) segmentation of a concrete specimen [21].

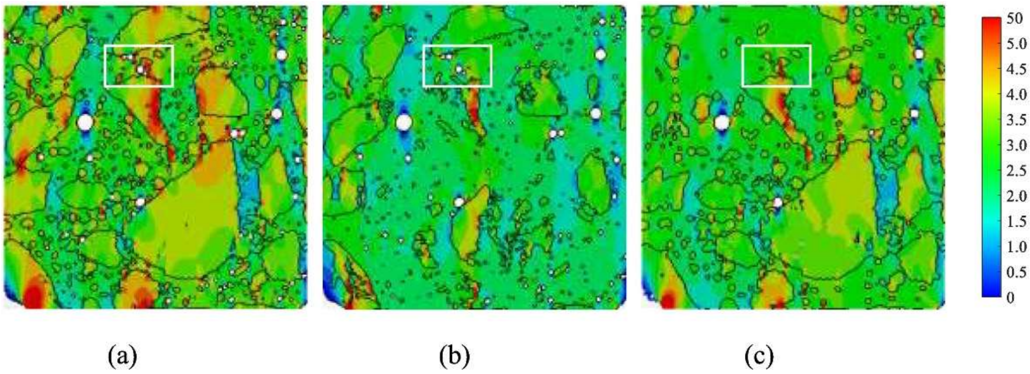


Figure 8: The stress field using the concrete microstructure obtained from the (a) combined X-ray and neutron CT, (b) X-ray CT, and (c) neutron CT under the uniaxial tension [21].

Administrative matters

The results were disseminated not only as lectures and publications, but also in form of media appearances, news on the ELKH website, and popular science journal articles. Four annual project workshops were also organized.

Finally, we thank the financial support of NKFIH and the commitment of our RADCON project partners which were essential for the success of this research.

Address: 29-33 Konkoly-Thege Miklós street, H-1121 Budapest, Hungary
Mailing address: P.O.B.: 49, Budapest, H-1525.
E-mail: szentmiklosi.laszlo@ek-cer.hu
Phone.: +36 1 392 2539
Web: www.ek-cer.hu

References:

1. Katalin Gméling, Veronika Szilágyi, Ildikó Harsányi, László Szentmiklósi: Hungarian fine-to-coarse aggregate, a possible constituent of near-vessel structural concrete of nuclear power plants, Construction and Building Materials (submitted), 2022
2. Szentmiklósi László, Maróti Boglárka, Párkányi Dénes, Harsányi Ildikó, Révay Zsolt: High-energy detector calibration data for k0-Neutron Activation Analysis, Journal of Radioanalytical and Nuclear Chemistry 315 (3) 743-750, 2018
3. László Szentmiklósi, Zoltán Kis, Boglárka Maróti and László Zoltán Horváth: Correction for neutron self-shielding and gamma-ray self-absorption in prompt-gamma activation analysis for large and irregularly-shaped samples, Journal of Analytical Atomic Spectrometry 36, 103 – 110, 2021
4. Szilágyi V., Gméling K., Józsa S., Harsányi I., Szentmiklósi L.: Oligomictic alluvial aggregates: petro-mineralogical and geochemical evaluation of sandy gravel formations on the middle course of the Danube (Hungary), Bulletin of Engineering Geology and the Environment 80: (8) pp. 5957-5977., 2021
5. Juhász Alexandra: Északnyugat magyarországi homokminták nehézásványainak nyomelem-összetétel vizsgálata Neutronaktivációs Analitikai (NAA) módszerrel, BSc dsszertáció, Eszterházy Károly Egyetem, 2020
6. Szilágyi V, Gméling K, Kis Z, Harsányi I, Szentmiklósi L: Neutron-based methods for the development of concrete., Proc. 12th Brittle Matrix Composites Conf., 183-194, 2019, Warsaw, Poland., 2019
7. J. Dragomirova, M.T. Palou, K. Gmeling, V. Szilágyi, I. Harsányi, L. Szentmiklósi: Design of heavyweight concrete used in radiation protection based on complete NAA, PGAA and XRF results. Activation and physical properties., Proc. 12th Brittle Matrix Composites Conf., 195-210, 2019, Warsaw, Poland., 2019
8. J. Dragomirová, M. T. Palou, E. Kuzielová, M. Žemlička, R. Novotný, K. Gméling: Optimization of cementitious composite for heavyweight concrete preparation using conduction calorimetry, Journal of Thermal Analysis and Calorimetry 142, 255–266(2020), 2020
9. D. Jóźwiak-Niedźwiedzka, A. Antolik, K. Dziedzic, K. Gméling, K. Bogusz: Laboratory investigations on fine aggregates used for concrete pavements due to the risk of ASR, Road Materials and Pavement Design, 22 (12), (2021), 2883-2895
10. D. Jóźwiak-Niedźwiedzka, K. Gméling, I. Harsányi, K. Dziedzic, M. A. Glinicki: Assessment of long-lived residual radioisotopes in cement induced by neutron radiation., MATBUD 2020 MATEC Web conferences 322 01019 (2020), 2020
11. Jóźwiak-Niedźwiedzka, D.; Gméling, K.; Antolik, A.; Dziedzic, K.; Glinicki, M.A.: Assessment of Long Lived Isotopes in Alkali-Silica Resistant Concrete Designed for Nuclear Installations, Materials 14, 4595, 2021
12. Janette Dragomirová, Martin T. Palou, Katalin Gméling, Veronika Szilágyi, Ildikó Harsányi, László Szentmiklósi: Experimental Study of Selected Properties of Heavyweight Concrete Based on Analysis of Chemical Composition and Radioactive Elements of its Components, Solid State Phenomena, Vol. 321, pp 113-118, 2021
13. Harsányi, I., Horváth, A., Kis, Z., Gméling, K., Jozwiak-Niedzwiedzka, D., Glinicki, M.A., Szentmiklósi, L. Assessment of neutron-induced activation of irradiated samples in a research reactor. Nuclear Engineering and Technology. (under peer review)
14. D. Hajdú, E. Dian, K. Gméling, E. Klinkby, C.P. Cooper-Jensenc, J. Osán, P. Zagyvai: Experimental study of concrete activation compared to MCNP simulations for safety of neutron sources, Applied Radiation and Isotopes 171 109644, 2021
15. Kis Zoltán: A Budapesti Kutatóreaktor 2. sz. vízszintes csatornájához tartozó biológiai védelem optimális átalakítását támogató Monte Carlo szimulációk eredményei a dózisteljesítmények vonatkozásában, EK belső riport, 2022. július
16. Yuliia Khmurovska, Petr Stemberk, Tamas Fekete: Mechanical response of biological shielding ring to variations in azimuthal neutron flux distribution, 23rd International Scientific Conference MECHANIKA 2018, 83-88, 2018
17. Y. Khmurovska: Influence of Neutron and Gamma Irradiation on Concrete Properties and Mechanical Performance, PhD Thesis, Czech Technical University in Prague, 2019
18. Y. Khmurovska, P. Štemberk, M. Petrik, J. Zak, V. Zacharda, V. Szilágyi, Z. Kis, I. Harsányi: Equipment for Concrete Irradiation Experiments, Proc. 24th Internat. Conf. MECHANIKA 2019, 2019
19. Y. Khmurovska, V. Szilágyi, P. Štemberk, Z. Kis, I. Harsányi, S. Sikorin, Y. Kaladkevich, E. Pavalanski, V. Fatseyeu: Water absorption test accompanied by dynamic neutron radiography of gamma-irradiated cement samples, Proceedings of the 12th Brittle Matrix Composites Conference, 2019

Address: 29-33 Konkoly-Thege Miklós street, H-1121 Budapest, Hungary
Mailing address: P.O.B.: 49, Budapest, H-1525.
E-mail: szentmiklosi.laszlo@ek-cer.hu
Phone.: +36 1 392 2539
Web: www.ek-cer.hu

20. Y. Khmurovska, P. Štemberk, T. Fekete, T. Eurajoki: Numerical analysis of VVER-440/213 concrete biological shield under normal operation., Nucl. Eng. Design, 350, 58-66., 2019
21. Kim HT, Razakamandimby RDFT, Szilagyi V, Kis Z, Szentmiklosi L, Glinicki MA, Park K: Reconstruction of concrete microstructure using complementarity of X-ray and neutron tomography, Cement and Concrete Research 148: 106540, 2021
22. Glinicki, M.A, Antolik, A., Kim, H.-T., Razakamandimby, Park, K., D.F.T., Szilágyi, V., Kis, Z., Dąbrowski, M. (in preparation) Enhanced tools for air void system characterization in concrete using X-ray microtomography, neutron tomography and optical microscopy.

Address: 29-33 Konkoly-Thege Miklós street, H-1121 Budapest, Hungary
Mailing address: P.O.B.: 49, Budapest, H-1525.
E-mail: szentmiklosi.laszlo@ek-cer.hu
Phone.: +36 1 392 2539
Web: www.ek-cer.hu