# NMR characterization of the permeability and structure of Boda Claystone Formation (BCF)

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**Summary**

High-level radioactive waste can be safely disposed of in deep geological repositories, for which a possible geological environment in Hungary is the Boda Claystone Formation. In the repository site selection, the geochemical investigation of the host rock is necessary including the structural characterization. In this study, the porosity (p%~1.5% and 5.84%) and the $T_{2cutoff}$ value (0.12 ms and 0.10 ms) of two siliciclastic rocks was determined by desktop low-field NMR, the value of which differed from the 3 ms accepted for clay-bound water and the 33 ms for movable water in clastic reservoirs. Based on the $T_{2cutoff}$, the producible porosity was found to be high, however, based on the $T_2$ distributions, the bound-water types dominate the composition of the water phase of the rock.

**Keywords:** deep geological repository, reservoir rock, $T_{2cutoff}$, NMR

## A Bodai Aleurolit Formáció (BAF) permeabilitásának és szerkezetének NMR jellemzése

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**Összefoglalás**

Magyarországon a nagy aktivitású radioaktív hulladékok végső elhelyezése még nem megoldott probléma. Az IAEA ajánlásai alapján az ilyen hulladékok hosszútávú és biztonságos elhelyezése mély geológiai tárolókban valósítható meg, melynek kiválasztása folyamatban van. Az országos felmérés (screening) alapján a Bodai Aleurolit Formáció (BAF) bizonyult a legígéretesebb kőzetnek, melynek széleskörű jellemzése elengedhetetlen a tároló kialakításához. A tároló kőzet pórusszerkezetének, kötött és mobilis víztartalmának, permeábilitásának vizsgálata fontos a kőzet radionuklid visszatartó képességének szempontjából, valamint szükséges bemenő adatokat szolgáltat a radioaktív hulladéktároló létesítmények biztonsági elemzéséhez szorosan kapcsolódó modellszámításokhoz. Munkánk során kisterű mágneses magrezonanciás módszerekkel (NMR) jellemeztünk két különböző mélységből származó furatmintát (BCF1 és BCF2). A mintákban található víz $T_2$ relaxációs ideje alapján meghatároztuk a különböző víztípusokat és az általuk kitöltött pórusok méretét és arányát. Jellemzően három víztípust tudtunk elkülöníteni: az agyagos fázishoz kötött vizet (51-77%, d ~ 0.6 nm), a kapillárisokban kötött vizet (20-43%, d ~ 2-40 nm) és a nagyobb pórusokat kitöltő eltávolítható vizet (3-6%, d ~ 200-400 nm). A modell oldattal telített kőzetminták $T_2$ relaxációs idő eloszlásai alapján meghatároztuk azok porozitását (P%~1,5% és 5,84%), melyek jó egyezést adtak a korábban He- piknométerrel és Hg porozimetriásan meghatározott értékekkel. A kőzet permeábilitására utaló és a kötött-mobilis vizek arányát jellemző $T_{2cutoff}$ értékeket (0,12 ms és 0,10 ms) a mintákat oldattal telítve, majd 105°C-on történő szárításukat követően ezek jellemzéséből határoztuk meg. Az így kapott értékek eltérnek az irodalomban törmelékes kőzetekre elfogadott 33 ms-tól, illetve a kőzetek agyagos fázisához tartozó 3 ms-tól. A $T_{2cutoff}$ alapján meghatároztuk a mobilis–kötött víz arányát (FFI/ BVI), mely alapján a minták nagy mennyiségben tartalmaznak eltávolítható vizet, azonban

a T$_2$ eloszlások alapján a kötött víztípusok a dominásnak. A T$_{2cutoff}$ értékét és az FFI / BVI arányát jelentősen befolyásolhatja a kőzet szárításának módja, mivel a magas hőmérsékleten való szárítás az agyagos fázis vízvesztéséhez vezethet, mely így befolyásolhatja a minta száraz állapotú porozitását. Ezentúl, NMR MoUSE segítségével, egy még vákuumcsomagolt kőzetminta esetén elvégeztük annak felületi térképezését, mellyel el tudtuk különíteni az eltérő víztartalmú, ásványi összetételű részeit a furatmintának.

**Kulcsszavak:** mélységi geológiai radioaktívhulladék-tároló, tároló kőzet, $T_{2cutoff}$, NMR

## Prefaces

The safe and long-term storage of high-level radioactive wastes demands deep geological repositories where the low porosity and permeability are crucial requirements. The Boda Claystone Formation is an outstanding candidate for this purpose and thus its geochemical investigation is an ongoing process. Low-field nuclear magnetic resonance (NMR) methods provide a simple and fast way for the characterization of porous rocks; the pore structure, pore sizes, water mobility, permability, and mineral composition, through the study of the confined liquids. In this study we demonstrate the strength of liquid phase, low-field NMR relaxometry through the comparison of the pore sizes and the $T_2$ cutoff values of two BCF borehole samples taken from different depths. Beside NMR relaxometry Vanda Papp applies NMR cryoporometry and diffusiometry techniques for cement-based composites, and geopolymers used as binders in the conditioning of low- and medium-level radioactive waste. The joint use of these methods is unique in the characterization of porous materials in liquid phase, the solid-liquid interface, and the movement of the liquid in the pore structure.

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The safe disposal of spent fuel and other high-level radioactive waste generated during the nuclear energy production is extremely important for the future generations. The selection of reliable host rocks suitable for long-term and safe storage is an important and current challenge worldwide, and Hungary is not an exception. The water content and water permeability of the potential host rock is a critical factor and should be known for total characterisation of the rock. As a result of the current research work, we were able to perform low-field NMR measurements on claystone matrices and to determine the $T_{2cutoff}$ value, which is a defining characteristic of the rock's porosity and suitability for receiving radioactive waste. The method was not available in Hungary before this research. The developed analytical method was successfully demonstrated by testing the Boda Claystone Formation (BCF), which is currently the most promising for the disposal of high-level radioactive waste.

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## 1. Introduction

*"Where half the electricity comes from"* can be read on the website of the Paks Nuclear Power Plant (NPP). In Hungary, according to surveys by the Hungarian Central Statistical Office, in 2022 nuclear energy accounted for about 50% of electricity production, which provided consumers with safe, cheap, and environmentally friendly electricity *(Hungarian Central Statistical Office n.d.)*. However, during the operation and decommissioning of nuclear power plants, which are a greener alternative to energy generation, waste is generated that must be handled according to appropriate safety guidelines. The main source of radioactive waste is the operation of the Paks NPP, smaller quantities are produced by other users of radioactive isotopes. Radioactive waste can be defined as materials that are either radioactive or contaminated with radioactivity and are no longer suitable for further use (*Ojovan–Lee–Kalmykov 2019*). Based on *IAEA Safety Standards Series No. GSG-1* about the *Classification of Radioactive Waste,* the generated nuclear waste can be classified into six groups according to the half-lives and radioactivity of the isotopes (exempt waste, very short-lived waste, very low-level waste, low-level waste, intermediate-level waste, and high-level waste). The way of conditioning and disposal of the radioactive wastes differs by categories.

According to the *National Programme of Hungary on the management of spent fuel and radioactive waste (2016)*, if the heat development of the waste during disposal is negligible, the waste can be classified as low- (LLW) or intermediate-level waste (ILW). The critical heat development value from the point of view of temporary storage and/or final disposal is 2 kW/m³, that is defined in the *MSZ 14344-1:2004 Standard*. Above this value the waste is high-level waste (HLW), and the heat development must be considered during its disposal. The purpose of radioactive waste disposal is defined in the *IAEA Safety Standards Series No. SSG-23* about the *Safety Case and Safety Assessment for the Disposal of Radioactive Waste* as follows: *"Disposal of radioactive waste represents the final step in its management, and disposal facilities are designed, operated and closed with a view to providing the necessary degree of containment and isolation to ensure safety. The fundamental safety objective is to protect people and the environment from harmful effects of ionizing radiation."*

In Hungary, the *Act CXVI of 1996 on Atomic Energy* states that the provision of the storage and final disposal

of radioactive waste is a state duty, and must be carried out by a government-appointed institution. This institution is the Public Limited Company for Radioactive Waste Management (PURAM), that coordinates the operation of Radioactive Waste Treatment and Disposal Facility (LLW, ILW), National Radioactive Waste Repository (LLW, ILW), Spent Fuel Interim Storage Facility and in addition, it designates a site for the disposal of high activity and long-lived radioactive waste and spent fuel (*National Programme of Hungary 2016)*. The disposal of low- and intermediate-level waste is already solved in Hungary in two repositories (near-surface and underground). The interim storage of high-activity waste (spent fuel) is possible in the Spent Fuel Interim Storage Facility near the nuclear power plant, while for the disposal site of a deep geological repository is under selection (*National Programme of Hungary 2016)*.

According to a broad international agreement, the final disposal of high-level waste can be safely solved in a deep geological repository, which is a facility, built hundreds of meters deep. The function of the repository is to protect the disposed waste from surface effects and processes and guarantees a stable geological environment for long-term safety. In 2000, PURAM set up a formation-qualifying research program (screening) covering the entire territory of the country. Based on the national screening the Boda Claystone Formation (BCF) was found to be the most promising, while Kiscelli Clay Formation was ranked second (*National Programme of Hungary 2016)*. During the selection procedure, the possible storage rocks must be considered according to several aspects. In the *IAEA Safety Standards Series No. SSG-14.* about the *Geological Disposal Facilities for Radioactive Waste,* these aspects to be examined are collected. To host the repository facility and to inhibit the radionuclides from entering the environment, the host geological setting should have favorable chemical, physical, geometrical, mechanical properties and be a uniform rock formation in comparatively simple geological environment. Here, we would like to highlight the physicochemical and geochemical aspects, which influence, among other things, the retardation properties of the host rock for the leaching of long-lived radionuclides. The retardation properties depend highly on the composition and pore structure of the rock, which affect the possible transportation process of the radionuclides by the ground water. Therefore, the structure and the permeability of the selected host rock are essential to be examined.

In 2004, PURAM prepared and authorized a research program for the designation of a site suitable for the disposal of high-activity and long-lived radioactive waste in Hungary and an underground research laboratory in Western Mecsek. In 2018, in accordance with the new legal regulations, PURAM prepared the framework program for the site investigation of BCF, which was approved in 2019. At the same time, a research paper was published about the results achieved (*Bernáth et al. 2018*), where the above-mentioned pore structure properties were also investigated. The porosity and permeability were characterized by NMR logging measurements, and it was found that the porosity, bulk water content and permeability are mainly related to cracks and cracked zones of the rock (*Bernáth et al. 2018*).

NMR logging tools are well suited for the in-situ investigation of conventional rocks, but their application to non-conventional rocks is still under research. In such cases, the physical parameters of the rock determined by desktop NMR methods, such as permeability and bound water content, can be used to calibrate the in-situ measurements (*Coates–Xiao–Prammer 1999*). These techniques are related to the significant magnetic moment of certain nucleons, in geophysics mainly to the magnetic moment of the protons in the pore space. The magnetic spins of the protons can be excited with radiofrequency impulses, which is followed by their return to the equilibrium state due to various relaxation processes. The relaxation from the transverse plane can be described by the transverse (spin-spin) relaxation time constant ($T_2$), the value of which depends on the mobility of the water protons. In the case of more bound water, the $T_2$ relaxation time is short, since the effect of the surface enhances the relaxation process, while a longer relaxation time can be measured for water filling larger voids. It is possible to distinguish water types with different mobilities based on their $T_2$ relaxation time values, and to determine their amount since the NMR signal intensity is proportional to the amount of water (*Papp et al. 2023*). Generally, in the case of rocks, the relaxation process of the liquid is influenced by 3 factors: the surface relaxation ($T_{2s}$), the bulk fluid processes ($T_{2\mathrm{bulk}}$) and the diffusion mechanisms of the fluid ($T_{\mathrm{diff}}$), however, in homogeneous magnetic fields, the latter can be neglected (*Testamanti- Rezaee 2017*). In the case of a fast exchange process, the total relaxation process of the system can be described by the weighted average of the relaxation rates ($1/T_2$) of water domains with different mobility:

$$\frac{1}{T_2} = \frac{V_s}{V}\frac{1}{T_{2s}} + \frac{V_{bulk}}{V}\frac{1}{T_{2bulk}} \qquad (1)$$

where $V$ is the total volume of the measurable water, $V_s$ and $V_{\mathrm{bulk}}$ are the volumes of the surface water and the bulk water respectively. $T_2$ is the observed apparent transverse relaxation time, while $T_{2\mathrm{bulk}}$ and $T_{2s}$ are the characteristic relaxation time constants of water molecules in the bulk-like and surface regions respectively (*Kimmich 1997*).

The total NMR porosity of the rock sample can be calculated from the intensity of the measured $T_2$ decay curves and the derived $T_2$ distribution curves (inverse Laplace transformation) can be directly calibrated to the porosity (*Coates–Xiao–Prammer 1999*). The total poros-

ity of a rock consists of the non-evaporable clay-bound water, the capillary-bound water and the movable water located in different sized pores (see in *Figure 1*) from which different porosities can be defined.
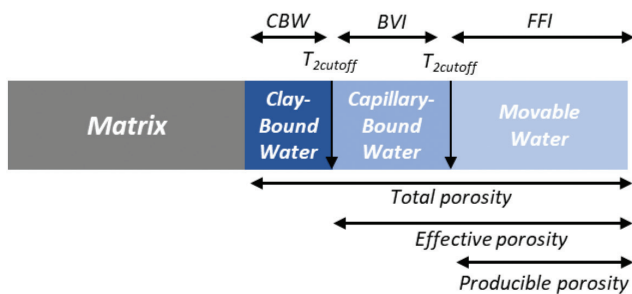


**Figure 1** | The composition of a rock with the porosities determined by the water domains. The two typical $T_{2cutoff}$ values distinguish the movable and non-movable water domains as well as the non-evaporable clay-bound water and the capillary-bound water

Source: The Authors' own figure based on Coates–Xiao–Prammer 1999

From the point of view of the host-rock selection procedure, the most important parameters are the free-fluid index (*FFI*) and the bulk volume irreducible (*BVI*), the ratio of which refers to the permeability of the rock. These can be determined from the so called $T_{2cutoff}$ value, which is the $T_2$ value below which the corresponding fluids are expected to be bound (*BVI*) and above which the fluids are expected to be movable (*FFI*) (*Coates–Xiao–Prammer 1999*). There is a possibility to determine a $T_{2cutoff}$ value for the clay-bound water as well, however, in this case the $T_2$ relaxation time constants of the clay- and capillary-bound water domains usually overlap, thus there is no sharp division between the two (*Coates–Xiao–Prammer 1999*). The $T_{2cutoff}$ value can be derived from the intersection of the cumulative porosities of the rock in dry and water-saturated states. Different rocks are often characterized by an exact $T_{2cutoff}$ value, although many factors can influence it (e.g., capillary pressure, lithology, pore characteristics, paramagnetic impurities) (*Coates–Xiao–Prammer 1999*).

The NMR MoUSE (Mobile Universal Surface Explorer) is a small, portable magnet that can be used in-situ, similarly to the NMR logging tools. Its advantage is that larger samples can be placed on its surface, and thus measured as a monolith, without any destruction or preparation. Due to the one-sided magnet, there is a gradient in the magnetic field moving away from the surface of the magnet, which provides an inhomogeneous magnetic field, allowing the study of molecular processes taking place in the system by using simple sequences. The disadvantage of the device is the relatively low sensitivity (*Blümich et al. 1998*).

In this study, two borehole samples of Boda Claystone Formation (BCF) were investigated by low-field NMR in dry and water-saturated state. The aim was to deter-

mine the $T_{2cutoff}$ value of this siliciclastic rock, to distinguish the irreducible bulk volume and the producible porosity, which are important input data for model calculations closely related to the safety analysis of radioactive waste storage facilities. NMR MoUSE measurements were carried out for surface mapping of the borehole samples, which provides information about the distribution of different siliciclastic phases of the rock.

## 2. Experimental and data evaluation

### 2.1. Materials, sample preparation

The studied boreholes of Boda Claystone Formation (BCF) were taken from two depths, 665.45 m (BCF1) and 746.06 m (BCF2). The diameter of the borehole was ~6 cm, and the samples were packed into foil.

For the NMR relaxometry measurements, cylinders (d ~ 7 mm) were drilled out of the two borehole samples using a rose drill under water cooling. In our preliminary studies the core samples (BCF1 and BCF2) were examined in monolith, powdered, and crushed forms, among which the monolith forms were the most promising, since the pore structure of the powder samples significantly changed. During the preparation of the samples, we observed that the BCF1 and BCF2 samples are visually different: the surface of the BCF1 sample is greyish, dried out quickly after unfolding, while the BCF2 sample is reddish in color, slightly shiny and did not show any significant changes after unfolding.

The liquid in which the samples were immersed was a model solution prepared according to the composition of the pore liquid of BSF. To achieve the concentrations listed in *Table 1*, $CaCl_2 \times 2H_2O$, $MgSO_4 \times 7H_2O$, $K_2SO_4$, $NaHCO_3$ and $Na_2HPO_4 \times 12H_2O$ salts (Sigma Aldrich, Merck) were dissolved in calculated amounts. Further components in ppb concentration were ignored as they do not influence the results of the NMR relaxometric measurements. The pH value of 8.8 of the resulting so-

**Table 1** | Composition of the model solution used to saturate the tested BAF samples

| Components | Concentration |
|---|---|
| | mg/dm³ |
| $HCO_3^-$ | 717 |
| $CO_3^{2-}$ | <3 |
| $SO_4^{2-}$ | 150 |
| $Cl^-$ | 14 |
| $PO_4^{3-}$ | 0.13 |
| Ca | 8.3 |
| K | 4.57 |
| Mg | 2.9 |
| Na | 254 |

Source: PURAM

lution was adjusted with sulfuric acid (Sigma Aldrich, ACS reagent, 95.0–98.0%) to the desired value of 8.1. The added sulfuric acid contributed to the sulfate concentration.

For the dry tests, the samples were dried in air for several days and then in an oven at 105 °C for 2 days. The removal of mobile water was followed by weighing, and the relaxometric measurements were performed after the constant mass to three decimal places was reached (the mass change of the samples was only 0.1–0.2 mg at the end of drying). The samples were placed into 15 mm wide glass NMR tubes.

For the measurements in saturated state, the samples were immersed and soaked in the prepared model solution for 3 days. A double amount of model solution (~4 ml) was poured onto the dry samples, and the samples were placed under vacuum in order to fully saturate the porous structure. We followed the mass change of the sample during the soaking, and after reaching a constant mass, the samples were taken out from the solution, and we measured the transverse ($T_2$) relaxation time constants of the water in the samples. Immediately before the $T_2$ relaxometric measurements, water was carefully wiped off from the surface of the cylindrical samples, and then we placed them in glass NMR tubes with a diameter of 15 mm. The length of the measurement took approx. 85 minutes, during which the samples apparently did not dry out.

## 2.2. Relaxometric measurements – Determination of the cut-off

A Minispec Bruker mq20 20 MHz relaxometer was applied for the measurements of relaxation times at room temperature (25 °C). The $T_2$ transverse relaxation time constants were measured using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence, consisting of a 90° pulse followed by a series of 180° pulses, while increasing the number of repetitions of the waiting time between pulses. The 90° pulse length was 2 µs. The transverse relaxation was measured with 512 transients to minimalize the uncertainty from low water content. 0.08 ms echo time was applied in every experiment to get as much information as possible about fast-relaxing, more bound water types (this is the smallest value of our device). We set the number of echoes to 1,000 to achieve the complete relaxation. The relaxation delay time was set to 10 s to detect all water domains in the samples. The receiver gain varied between 59–95 dB according to the water content of the samples. Due to the low water content of the samples, the NMR signal of the glass tube had to be considered, with which the primary data of the samples were corrected.

A volume calibration was carried out to calculate the porosity of the samples. $T_2$ measurements were performed on model solutions with volumes between 200 and 1,000 µl, and the initial intensity of the $T_2$ exponential decay curves were plotted as a function of the volume. The equation of the fitted linear can be used to specify the amount of liquid in the BCF samples, i.e., the pore volume ($V_p$). Based on the dimensions of the cylindrical samples, we calculated the total volume ($V_t$), thus the porosity ($P\%$) of the samples could be obtained using Equation 2.

$$P\% = \frac{V_p}{V_t} \tag{2}$$

The primary data series (signal intensity as a function of time) were corrected with the intensity change resulting from the receiver gain value used during the measurements (a change of 6 dB causes a 2-fold change in the intensity), and with $y_0$ to 0. The intensity values were converted to porosity as described above, and then the exponential curves were evaluated with the MERA (Multi Exponential Relaxation Analysis) fitting program running under the Matlab software based on inverse Laplace transformation. During the evaluation, we obtained a $T_2$ time distribution curve, where the maxima indicate the relaxation times characteristic of the given types of water, while the area under the curve is proportional to the amount. During the evaluation, the individual data series were fitted with 300 exponentials, in a time interval of 0.08–10000 ms, using the Chi-square method. The intensity-time curves were also fitted with the sum of exponential functions with the OriginPro software based on the least squares method for verification.

To determine the $T_{2cutoff}$ value, the $T_2$ distribution curves were numerically integrated with the OriginPro software to obtain cumulative curves, the maximum value of the relative scale of which was adjusted to the total porosity. The intersection point of the line drawn to the saturation value of the cumulative curves in the dry state and the cumulative curve belonging to the saturated sample gave the $T_{2cutoff}$ value, as detailed above.

## 2.3. NMR MoUSE measurements: surface mapping

The BCF1 and BCF2 claystone samples were examined in vacuum-packed state and after unpacking, and the characteristic relaxation times of the samples were determined with the aforementioned desktop magnet. The surface of the BCF1 sample in vacuum-packed state was studied at 16 points, thus a two-dimensional "map" of the sample was created *(Figure 2)*.

No special sample preparation happened before the NMR MoUSE measurements. During mapping, the surface of BCF1 sample was divided into 16 parts of 1.5 cm, adjusted to the detection window of the device. For accuracy, we also measured the material of the vacuum package.

The applied mobile probe head contains a permanent magnet, the detection depth of which was 3 mm, and

**Figure 2** | The NMR MoUSE instrument and the vacuum-packed BCF1 sample

Source: The Authors' own photo

the gradient field strength was ~5.5 T/m. The borehole was placed onto this detection window, and its location was changed to carry out the mapping of the surface. During the measurements, we used the CPMG pulse sequence, similarly to the cut-off measurements. The transverse relaxation of water in the packed and unpacked boreholes was measured three times to ensure reproducibility. In each case, we measured 30,000 transients with the same echo time (0.08 ms). During the mapping of the BCF1 sample, we performed one measurement at each coordinate point, recording 15,000 transients. The large number of transients was reasonable due to the low sensitivity of the device and the low water content of the samples. The number of echoes varied between 100–250 to achieve the complete relaxation. The delay time was set to 0.5 s for both samples and the receiver gain to 107 dB.

The primary data series were evaluated with the MERA (Multi Exponential Relaxation Analysis) fitting program written on the Matlab interface, which is based on the inverse Laplace transformation, similarly to the relaxometric measurements. The exponential decays were approximated with 300 exponentials, in a time interval of 0.06–100 ms, using the Chi-square method. The results were also evaluated with the method of least squares (Origin ©) for verification. During the mapping, we created a two-dimensional data matrix from the characteristic $T_2$ relaxation times according to the coordinate system drawn on the sample.

# 3. Results and discussion

## 3.1. Determination of the $T_2$ cut-off values

*Saturated samples*
Generally, three different water domains can be distinguished in water saturated rocks: the clay-bound water, the capillary-bound water and the movable water *(Figure 1)*. These water domains can fill out different sized pores in the rocks and consequently, they can be distinguished based on their transversal relaxation times. The transversal relaxation of water is faster in smaller pores, where the mobility of water molecules is lower, while in the case of larger pores the relaxation process takes longer. *Figure 3A* shows the $T_2$ relaxation time distribution curves of the BCF1 and BCF2 claystone samples. Based on these $T_2$ distribution curves, we were able to distinguish four types of water with different mobility, which can be assigned to pores of different sizes, observed previously by independent methods (*Fedor et al. 2018*), as follows: the domain belonging to 0.1 ms represents a very bound type of water, which can be interpreted as water bound to the clay mineral phase of the claystone (ultramicropores, $d < 1$ nm). The peak around 0.7–1.5 ms in BCF1 is also an immobile, rapidly relaxing domain, which may be assigned to water located in the micropores ($d < 2$ nm). This domain is represented by two peaks in the case of BCF2 (0.3–1.7 ms). The third domain appears at a relaxation time of around 3.6–7.3 ms, which time increase is the consequence of the larger pore size, which may be related to water filling the capillary pores (mesopores, 2 nm < $d$ < 50 nm). The last domain, visible around 50 ms, can be identified as water in the larger macropores ($d > 50$ nm).

The conversion of $T_2$ distribution curves to pore size distributions is possible by knowing the value of the surface relaxivity ($\xi$):

$$\frac{1}{T_2} = \xi \frac{S_p}{V_p} + \frac{1}{T_{2bulk}} \tag{3}$$

where $T_2$ is the observed apparent transverse relaxation time, $T_{2\text{bulk}}$ is the characteristic relaxation time constants of water molecules in the bulk phase, while $S_\text{p}$ is the surface and $V_\text{p}$ is the volume of the pores (*Allen–Stephenson–Stange 1997*). The value of the surface relaxivity depends on the thickness of the water layer ($\lambda \sim 0.3$ nm for water molecules) on the surface and the $T_2$ relaxation time of water molecules in this layer ($T_{2\text{s}}$) (*Allen–Stephenson–Stange 1997*). Since rocks are heterogeneous systems, they cannot be characterized by an accurate surface relaxivity value, and thus the pore size can only be estimated. For this estimation the previously determined $T_{2\text{s}} \sim 0.11$ ms and $\lambda \sim 0.3$ nm were used, the ratio of which provided the surface relaxivity ($\xi \sim 2.7$ nm/ms), while the pore geometry was assumed to be slit-like ($S_\text{p}/V_\text{p} = 2/d$). The pore size distribution of the two claystone samples is shown in *Figure 3B*. The determined
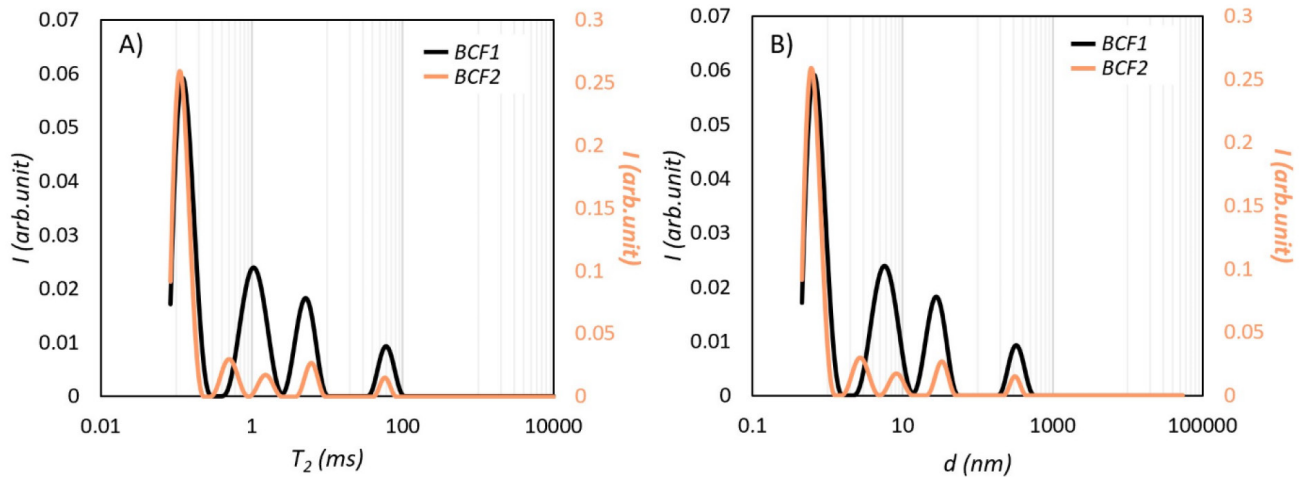
**Figure 3**    A) $T_2$ distribution curves and B) the derived size distribution curves of BCF1 and BCF2 samples in water saturated state

Source: The Authors' own figure

pore size values for the first water domain ($d \sim 0.6$ nm) indicate ultramicropores in the clay phase, while the second and third peaks can be assigned to the mesopores (probably capillary pores) of the rocks based on their pore sizes ($d \sim 2$–40 nm). The last peak indicates the macropores in the claystone samples ($d \sim 200$–400 nm).

Comparing the amplitude of the peaks the quantitative contributions of the pores can be deduced. In case of the BCF1 sample the ratio of the different pores is as follows: 51% ultramicropores (clay-bound water), 43% mesopores (capillary-bound water), 6% macropores (movable water). On the other hand, in the case of the BCF2: 77% ultramicropores (clay-bound water), 20% mesopores (capillary-bound water), 3% macropores (movable water), which means that this sample probably contains more clay mineral phases, retaining water more effectively. The slower drying phenomenon seen during the preparation of the samples can also support this conclusion. Furthermore, the two samples differ in terms of

the water content as well, as it can be seen on the two intensity scales in *Figure 3*. Beyond the proportion of different pores, and the water content (possible mineral composition), there is no significant difference between the pore structure of the two samples.

*Dried samples*

After drying the claystone samples to constant weight, the $T_2$ relaxation of the remained moisture content was measured again. The resulted $T_2$ relaxation time distribution curves are shown in *Figure 4* (orange curves) in relation to that of the saturated samples (blue curves). It can be observed that the intensity of the most bound type of water slightly changes due to drying, which confirms that this largely represents water strongly bound to the clay mineral component. The intensity of the water types with higher mobility decreases and their characteristic $T_2$ values increase, due to the evaporation of the water from the pores, as expected.
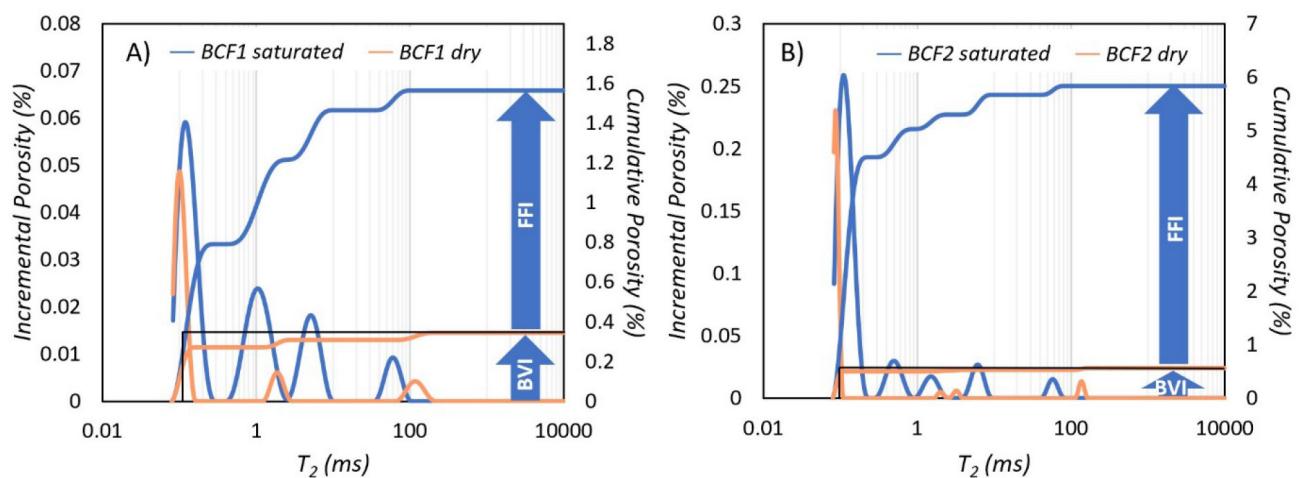


**Figure 4**    $T_2$ distribution curves and the derived cumulative curves of BCF1 (A) and BCF2 (B) in saturated and dry state, with the cut-off (black lines), the FFI and BVI values (arrows)

Source: The Authors' own figure

*T₂cutoff values*

*$T_{2cutoff}$ values*

The $T_2$ distribution curves were integrated to form cumulative distribution curves, which can be seen in *Figure 4*. The cumulative porosity scales on the right y axis show the effect of drying: for BCF1 the 1.56% shows the total porosity of the saturated sample, which is reduced to approximately the quarter of it (0.35%). *Fedor et al. (2018)* performed He-pycnometry and Mercury Intrusion Porosimetry measurements on other BCF samples and found that the porosity of the samples varied between 0.78–3%. The porosity values obtained from NMR are comparable with these. The maxima of the cumulative curves indicate the FFI (free-fluid index) and BVI (bulk volume irreducible, bound water) ranges, the ratio of which is therefore 1.21% / 0.35% = 3.45 in the case of BCF1. The total porosity of BCF2 is higher (5.84%), but this means the increased value of the FFI index, whose ratio to the BVI is 5.28% / 0.56% = 9.43.

The determined $T_{2cutoff}$ value is higher for BCF1 (0.12 ms) than for BCF2 (0.10 ms). Usually, $T_{2cutoff}$ value of 33 ms is accepted for sandstones, $T_{2cutoff}$ ~ 90–100 ms for carbonates and $T_{2cutoff}$ ~ 3 ms is commonly used to identify clay bound water (*Testamanti–Rezaee 2017*). However, the commonly accepted $T_{2cutoff}$ values are not always suitable for any observed rocks. Testamanti and Rezaee found that most of the transverse relaxation processes occur below 3 ms in saturated shale samples, thus the conventionally accepted clay bound water cut-off is unsuitable for shales. They received $T_{2cutoff}$ ~ 0.22 and 0.26 ms instead, and the ratio of FFI index / BVI index occured around 3 (*Testamanti–Rezaee 2017*). In our water saturated samples there can be observed relaxation domains above 3 ms, thus the deviation of the determined values from the literature cannot be explained this way. However, the influence of the drying temperature was also investigated in this publication and was found that high temperature can cause the temporary loss of the interlayer water in clays, affecting the pore structure permanently (*Testamanti–Rezaee 2017*). This structural change and water loss in the clay phase can result in a lower porosity, which can affect the determination of the $T_{2cutoff}$ value.

In our case, further experiments are necessary to explain the low $T_{2cutoff}$ values, to reveal any structural changes affecting porosity, and to decide if the values are suitable for separating FFI / BVI, or perhaps CBW/ (FFI+BVI).

## 3.2. NMR MoUSE measurements: surface mapping

Due to the lower sensitivity of the NMR MoUSE, only two relaxation domains were found in the samples, the characteristic $T_2$ times of which, $T_{21}$ ~0.2–0.3 ms and $T_{22}$ ~1–1.6 ms, are similar to those of more bound water types determined by the desktop relaxometer. In the dry state of the sample, their quantity is determinant, thus detectable with this method. Nevertheless, the NMR MoUSE can be especially suitable for a quick comparative measurement of samples, even in their packaged state.

The two claystone samples were measured first in the original vacuum packaging, and then after unpacking. Comparing the $T_2$ relaxation distributions, in the case of BCF1 the curve shifted to lower time values reflecting the fast drying of the surface, which was also visible, as mentioned above in in section *2.1. (Materials, sample preparation)*. For BCF2, the $T_2$ relaxation time distributions of the packed and unpacked samples are almost identical, which is also confirmed by the fact that the appearance of the BCF2 sample did not visibly change during unpacking.

To eliminate the effect of unpacking the surface mapping was carried out in the vacuum-packed state on BCF1 sample. The surface was divided into 16 parts (see *Figure 2*) and $T_2$ relaxation was measured at each point. The $T_2$ value, attributed to the less bound water in the rock, was plotted according to the coordinates on the surface. *Figure 5* represents the obtained $T_2$ map, on which a clearly visible shape is formed with higher relaxation time, parallelly to the surface of the mapped rock in the photo. The marked part of the rock, with the higher $T_2$ values, presumably contains more permeable minerals. Based on this, we can say that, despite its lower sensitivity, this method is suitable for fast examining the differences between samples, as well as for mapping the water distribution within the rock, and determining differences in mineral composition.
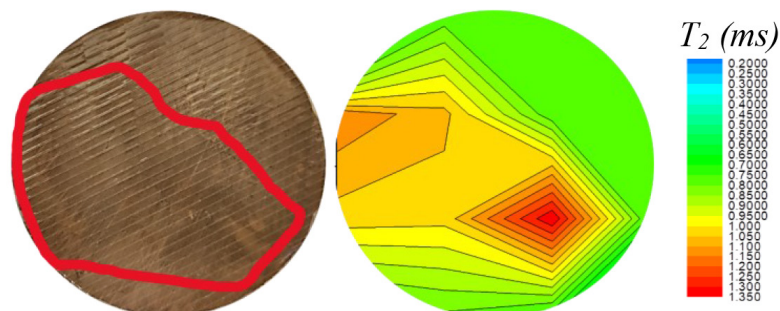


**Figure 5** | The photo of the examined surface of the packaged BCF1 sample compared to the T₂ surface map

Source: The Authors' own figure

# 4. Conclusion

In terms of the long-term and safe disposal of high-level radioactive waste, an important criterion is the qualification of the geological host rock of the repository. A crucial point of this qualification is the characterization of the pore structure, permeability, mobile and bound water content of the rock. The designated host rock in Hungary is the Boda Claystone Formation (BCF), which is a clayey rock with nanosized pores and extremely low porosity. Due to the outstanding properties of the rock, the use of conventional structural analysis techniques is difficult for the characterization. NMR is a promising alternative for this task, thanks to its sensitivity for the water protons, even in extremely small pores and bound state. The desktop NMR instrument can be used to easily determine the critical parameters (e.g., pore size, $T_{2cutoff}$, porosity) that can facilitate the in-situ investigation of a borehole. With this type of device, we successfully characterized the pore structure of two BCF borehole samples, determined the size and amount of the ultramicropores filled with clay-bound water, the mesopores saturated with capillary-bound water and the macropores containing movable water. The $T_{2cutoff}$ values were derived from the changes of the water types after drying, resulting in 0.12 ms and 0.10 ms, for BCF1 and BCF2, respectively. Based on the determined FFI / BVI ratios, the bound water content of the rocks is low, however, based on the $T_2$ distributions, they dominate the composition of the water phase of the rock (51–77% clay-bound water, 43–20% capillary-bound water). This ratio depends highly on the porosity of the samples; however, we have to be aware that the temperature of drying can significantly affect the observed porosity of the samples. In the case of a dry sample in its original vacuum packaging, the use of a one-sided magnet (NMR MoUSE) provided a $T_2$ surface map of the rock, where phases with higher water content and different compositions can be clearly distinguished.



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