



Article

Geological Risk Calculation through Probability of Success (PoS), Applied to Radioactive Waste Disposal in Deep Wells: A Conceptual Study in the Pre-Neogene Basement in the Northern Croatia

Tomislav Malvić ^{1,*}, Maria Alzira Pimenta Dinis ^{2,*}, Josipa Velić ¹, Jasenka Sremac ³, Josip Ivšinović ⁴, Marija Bošnjak ⁵, Uroš Barudžija ¹, Želimir Veinović ¹ and Hélder Fernando Pedrosa e Sousa ⁶

¹ Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Pierottijeva 6, HR 10000 Zagreb, Croatia; josipa.velic@rgn.hr (J.V.); uros.barudzija@rgn.hr (U.B.); zelimir.veinovic@rgn.hr (Z.V.)

² UFP Energy, Environment and Health Research Unit (FP-ENAS), University Fernando Pessoa, Praça 9 de Abril 349, 4249-004 Porto, Portugal

³ Faculty of Science, University of Zagreb Horvatovac 102a, HR-10000 Zagreb, Croatia; jasenka.sremac@geol.pmf.hr

⁴ INA-Industry of Oil Plc., Trg G. Szabe 1, HR-44310 Novska Zagreb, Croatia; josip.ivsinovic@ina.hr

⁵ Croatian Natural History Museum, Demetrova 1, HR-10000 Zagreb, Croatia; marija.bosnjak@hpm.hr

⁶ Department of Mathematics (DM.UTAD), University of Trás-os-Montes and Alto Douro, Quinta de Prados, 5001-801 Vila Real, Portugal; hfps@utad.pt

* Correspondence: tomlav.malvic@rgn.hr (T.M.); madinis@ufp.edu.pt (M.A.P.D.)

Received: 25 May 2020; Accepted: 27 June 2020; Published: 29 June 2020



Abstract: The basic principles of geological risk calculation through probability of success (PoS) are mostly applied to numerical estimation of additional hydrocarbon existence in proven reservoirs or potential hydrocarbon discoveries in selected geological regional subsurface volumes. It can be adapted and validated for a comprehensive input dataset collected in the selected petroleum province, by dividing up geological events into several probability categories and classes. Such methodology has been widely developed in the last decades in the Croatian subsurface—mostly in the Croatian Pannonian Basin System (CPBS). Through the adaptation of geological categories, it was also applied in hybrid, i.e., stochastic, models developed in the CPBS (Drava Depression), mostly for inclusion of porosity values. As the robustness of this methodology is very high, it was also modified to estimate the influence of water-flooding in increasing oil recovery in some proven Neogene sandstone reservoirs in the CPBS (Sava Depression). This new modification is presented to be applied to geological risk calculation, intending to assess the safety of geological environment storage in deep wells, where spent nuclear fuel (SPN) would be disposed, a subject of great importance. The conceptual study encompassed the magmatic and metamorphic rocks in the pre-Neogene basement of the CPBS, intended to be used for such purpose. Regionally distributed lithologies are considered for nuclear waste disposal purpose, in order to detect the safest ones, considering petrophysical values, water saturation, recent weathering and tectonic activity.

Keywords: geological risk; pre-Neogene basement; radioactive waste disposal; northern Croatia; probability of success (PoS)

1. Introduction

Probability of success (PoS) is a deterministic method by which deterministic estimation of independent categories within the hydrocarbon system are analyzed in potential or proven reservoirs or selected properties. The main independent categories are trap, reservoir, migration, source rock and preservation of hydrocarbons. These categories were determined on the basis of data from wells, logs, seismic interpretation, core analysis, stratigraphy and fluid production.

This has been a longstanding application of the PoS method in the Croatian Pannonian Basin System (CPBS). The first application in the CPBS was made on the example of Bjelovar Subdepression [1] for the member of the Moslavačka Gora Formation Bridge and the members of the Polo and Ashes of the Kloštar Ivanić Formation. Malvić [2] applied a deterministic–stochastic approach in the PoS calculation of Badenian clastites of the Stari Gradac–Barcs Nyugat field (Drava Depression). Malvić & Rusan [3] calculated the value of PoS for “basement rocks and Miocene breccias” and “Upper Miocene sandstone” from Bjelovar Subdepression. Stochastically improved methodology for PoS calculations for Stari Gradac–Barcs Nyugat field (Drava Depression) is proposed by Malvić & Velić [4]. The deterministic assessment of independent categories within the system analyses potential or proven reservoirs or selected properties (called custom geological probability). The mathematical expression for geological risk or geological probability (i.e., PoS, e.g., [1]) for hydrocarbon systems is presented in Equation (1):

$$\text{PoS} = p(t) \cdot p(r) \cdot p(m) \cdot p(sr) \cdot p(\text{CHp}) \quad (1)$$

where:

- PoS - geological probability of success (%);
- $p(t)$ - probability of potential traps (%);
- $p(r)$ - probability of reservoir characteristics (%);
- $p(m)$ - the probability of hydrocarbon migration (%);
- $p(sr)$ - the probability of the existence of source rocks (%);
- $p(\text{CHp})$ - the probability of hydrocarbon preservation (%).

Using the data indicated in Figure 1 and the mathematical Equation (1), the geological risk is calculated for each observed stratigraphic interval.

Novak Mavar [5] calculated the geological probability of preserving the CO₂ saturated reservoir in the Ivanić field (Sava Depression). The author made an assessment of the risk of migration through the sealing rocks of the oil–gas system into which CO₂ is injected, which was previously saturated with oil and/or methane. As the size of CO₂ and CH₄ molecules is approximately the same, a methodology for estimating the possibility of CH₄ migration through the same insulator rocks was used to determine the probability of CO₂ retention in the reservoir. The results of the calculation of the preservation probability of the Ivanić field reservoir “gamma series” indicate a certain event (the calculated value is 1.00). The obtained value is expected since it is an existing hydrocarbon deposit.

Malvić et al. [6] used the PoS method to calculate the probability of finding new gas discoveries in the wider area of Ivana and Ika gas fields (northern Adriatic, Croatia). Režić & Varenina [7] have designed a computer program for the calculation of PoS used for the probability assessment of new gas discoveries in the Croatian part of the Po Depression. The algorithm for calculating PoS in the northern Adriatic is shown in Figure 2. Values for PoS and p are selected as categorical probabilities within the 0–1 interval. According to the same authors, a PoS value of 0.2 is the cutoff value based on which it is decided whether or not further research will be conducted in the CPBS area for the Upper Miocene reservoirs. In any modification, where probability must be 100% (1.0), such cutoff should not be applied, but methodology itself could be. Consequently, PoS less than 1.0 is not suitable for nuclear waste disposal except if some risk for the selected variable in the long period (e.g., scale of 10⁶ years) would be legally considered and allowed. It could be done for example in case of radionuclides with shorter half-life cycle, or regional probabilities for variable active on long geological scale (e.g.,

fault activity in the last 1 or more Ma). In any case, probabilities less than 1.0 must be particularized in detail.

TRAP		RESERVOIR		SOURCE ROCKS		MIGRATION		HC PRESERVATION	
Structural		Reservoir type		Source facies		HC shows		Reservoir pressure	
Anticline and buried hill linked to basement	1.00	Sandstone clean and laterally extended; Basement granite, gabbro; Dolomites and Algae reefs (secondary porosity)	1.00	Kerogen type I and/or II	1.00	Production of hydrocarbons	1.00	Higher than hydrostatic	1.00
Faulted anticline	0.75	Sandstones, rich in silt and clay; Basement with secondary porosity, limited extending; Algae reefs, filled with skeletal debris, mud and marine cements	0.75	Kerogen type III	0.75	Hydrocarbons in traces; New gas detected >10 %	0.75	Approximately hydrostatic	0.75
Structural nose closed by fault	0.50	Sandstone including significant portion of silt/clay particles, limited extending;	0.50	Favourable palaeo-facies organic matter sedimentation	0.50	Oil determined in cores (luminescent analysis, core tests)	0.50	Lower than hydrostatic	0.50
Any "positive" faulted structure, margins are not firmly defined	0.25	Basement rocks, including low secondary porosity and limited extending	0.25	Regionally known source rock facies, but not proven at observed locality	0.25	Oil determined in traces (lumin. anal., core tests)	0.25		0.25
Undefined structural framework	0.05	Undefined reservoir type	0.05	Undefined source rock type	0.05	Hydrocarbon are not observed	0.05		0.05

Stratigraphic or combined		Porosity features		Maturity		Position of trap		Formation water	
Algae reef form	1.00	Primary porosity >15 %; Secondary porosity >5 %	1.00	Sediments are in catagenesis phase ("oil" or "wet" gas-)	1.00	Trap is located in proven migration distance	1.00	Still aquifer of field-waters	1.00
Sandstones, pinched out	0.75	Primary porosity 5-15 %; Secondary porosity 1-5 %	0.75	Sediments are in metagenesis phase	0.75	Trap is located between two source rocks depocentres	0.75	Active aquifer of field-waters	0.75
Sediments changed by diagenesis	0.50	Primary porosity <10 %; Permeability <1x10 ⁻³ (micrometer ²)	0.50	Sediments are in early catagenesis phase	0.50	Short migration pathway (<10 km)	0.50	Infiltrated aquifer from adjacent formations	0.50
Abrupt changes of petrophysical properties (caly, different facies)	0.25	Secondary porosity <1 %	0.25	Sediments are in late diagenesis phase	0.25	Long migration pathway (>10 km)	0.25	Infiltrated aquifer from surface	0.25
Undefined stratigraphic framework	0.05	Undefined porosity values	0.05	Undefined maturity level	0.05	Undefined source rocks	0.05		0.05

Quality of cap rock		Data sources		Timing	
Regional proven cap rock (seals, isolator)	1.00	Geochemical analysis on cores and fluids	1.00	Trap is older than matured source rocks	1.00
Rocks without reservoir properties	0.75	Analogy with close located geochemical analyses	0.75	Trap is younger than matured source rocks	0.75
Rocks permeable for gas (gas leakage)	0.50	Thermal modeling and calculation (e.g. Lopatin, Waples etc.)	0.50	Relation between trap and source rocks is unknown	0.50
Permeable rocks with locally higher silt/clay content	0.25	Thermal modeling at just a few locations	0.25		0.25
Undefined cap rock	0.05	Undefined data sources	0.05		0.05

Figure 1. Geological categories and subcategories of probability of success (PoS) (e.g., [4]).

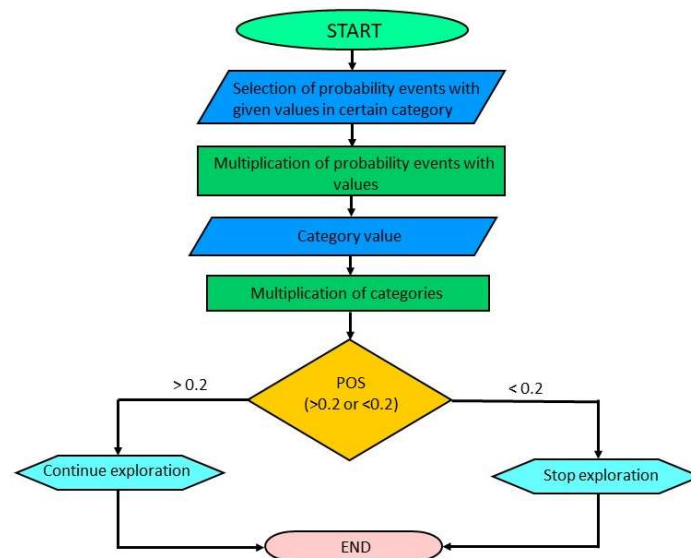


Figure 2. PoS algorithm of Režić & Varenina [7].

The methodology for determining geological probability was applied in calculating the persistence of the remaining economic quantities of hydrocarbons in the western part of the Sava Depression by Ivšinović [8]. This part of the Sava Depression is a relatively well-explored area with a large number of wells and discovered hydrocarbon reserves. The values of individual categories and subcategories of PoS are deterministically determined and PoS for the western part of the Sava Depression is 0.4218.

Recently, Malvić et al. [9] modified PoS was applied for assessment of water injection success in the western part of the Sava Depression. Consequently, PoS is considered as a very robust method for assessment of different subsurface rock–fluid–solid systems in deep boreholes. The disposal of high-level radioactive waste (HLW) in such deep wells is a part of the Croatian plan to safely dispose the spent nuclear fuel (SNF) from the Krško nuclear power plant. The national program for the implementation of the radioactive waste, disused sources and spent nuclear fuel disposal Strategy (program for the period until 2025 with a view to be extended until 2060; [10]) and the third revision of the decommissioning program and the Krško nuclear power plant (NPP) radioactive waste (RW) and spent nuclear fuel disposal program [11] predicts long-term storage of SNF from Krško NPP at the power plant located in the Municipality of Krško in Slovenia. The process of obtaining the necessary permits for such a storage site is ongoing. As a final solution for the disposal of SNF and/or HLW, the radioactive waste, disused sources and spent nuclear fuel disposal strategy [12] and the national program [10] envisage deep geological repository at a Croatia or Slovenia convenient location—or in the territory of the European Union, if an international landfill is established. If the disposal at a Croatia or Slovenia location is to be developed, probable host rock will be crystalline. The third revision of the decommissioning program proposes the utilization of the KBS-3 V disposal concept. The focus is given on deep geological repository with the recommendation to reconsider the possibilities of optimizing the proposed solution, as well as other technologies for disposal of SNF and/or HLW generated by processing or reprocessing of fuel from nuclear power plant “Krško” (Croat. abbr. NEK). One is deep boreholes disposal, which could be favorable regarding the volume of HLW, since the Slovenian/Croatian program is small, and Krško NPP has only one reactor with 1983–2043 operational span and less than 2 500 SNF assemblies [13]. The disposal program is planned to start in 2052.

Such national programs are done in many countries with nuclear energy facilities, e.g., the basic strategic to manage HLW and liquidation NPP is contained in the energy policy of the Slovak Republic (e.g., [14]). The goal is to solve, in the long run, deposition of HLW and SNF. The most important part of such a project is the disposal in deep subsurface rocks and the use of natural and artificial protectives to safely isolate HLW from the biosphere. Galamboš et al. [14] pointed out the clays as very suitable sealings, namely of bentonite type, and listed several deposits in the Slovak Republic, considering specific geotechnical properties involved.

Later, such work has been extended [15] in studying bentonite volume changes due to water content and using such property in the creation of artificial sealings in boreholes, especially for fillings of fractures in such volumes. Those two Slovakian studies clearly show that national nuclear energy policy and supporting experimental projects are of extreme importance for safely disposal and public response to nuclear energy in general.

2. Geological Samples of the Pre-Neogene Basement Rocks in Northern Croatia

Lithological properties of two characteristic groups of rocks in the pre-Neogene basement, sedimentary carbonates and metamorphic rocks, taken from the outcrops in Medvednica Mountains, are described, serving as the analogs for similar lithologies found in the deep wells of the CPBS. Geological relationships of the Neogene deposits and metamorphic rocks in the central part, as well as with sedimentary carbonate rocks in the southwestern part of the Medvednica mountains, are shown in Figure 3 [16].

Sedimentary carbonate rocks found in the pre-Neogene basement of the CPBS are mainly Middle and Upper Triassic marine limestones and dolomites, which are well described at the outcrops in Medvednica mountains [18–21], as well as in the neighboring Samoborska Gora and Žumberak [20–23].

Their clasts are regularly found as constituents in the overlying Neogene carbonate breccias. Pebbles of these rocks are also significantly incorporated in the Plio-Quaternary alluvial deposits of the Sava River [24]. Similar Middle Triassic rocks were also described as the Neogene basement rocks in the Papuk mountains [25], where Middle Triassic limestones and dolomites predominate.

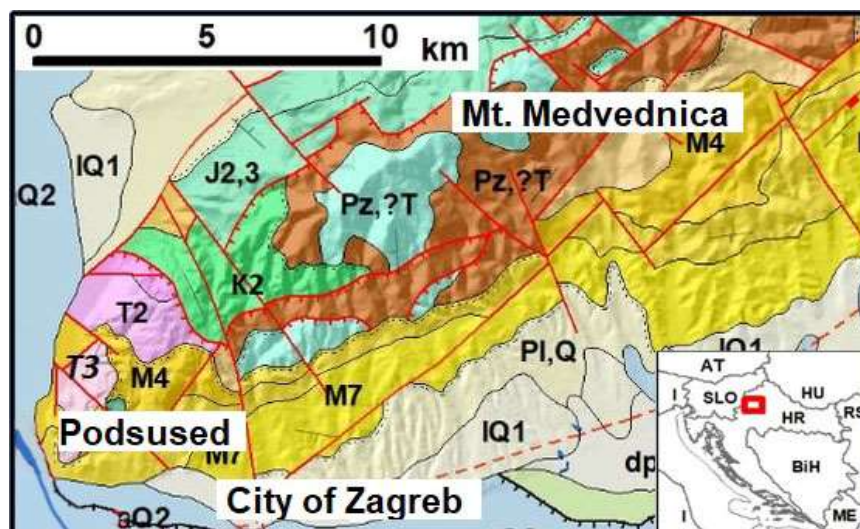


Figure 3. Geological relationships of the Neogene deposits and the pre-Neogene basement rocks in the central and SW parts of Medvednica mountains. Legend for geology, after [17]: Pz, ?T—Paleozoic to Triassic parametamorphites; T2—Middle Triassic limestones and dolomites; T3—Upper Triassic dolomites; K2—Upper Cretaceous carbonate clastics; M4, M7—Neogene deposits; Pl, Q, IQ1, Q2—Plio—Quaternary deposits.

Several lithofacies of Triassic dolomites were described in the Medvednica mountains as dark-gray dolomite, often intersected with secondary tectonic cracks and veins (Figure 4a) filled with carbonate cements and matrix, prevailing among carbonate lithotypes. This dolomite is heavily weathered, often cut up into small pieces and grinded up to the sand grain size. In a microscale, it shows fine-grained to medium-grained hipidiotopic dolomite texture (Figure 4b). It is often accompanied with dolomite breccias of different types and origin. These rocks show various types and significant volumes of secondary porosity, mainly of diagenetic or tectonic origin, as well as the combination of both [21,23].

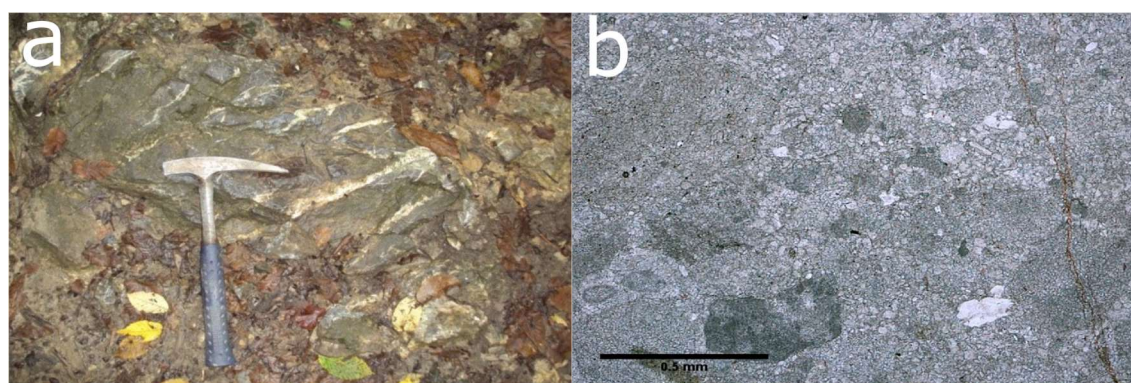


Figure 4. (a) Outcrop with dark gray dolomite in the Medvednica mountains; (b) photomicrograph of brecciated dark gray dolomite (width of the photomicrograph is 1.7 mm).

The light-colored crystalline dolomite is almost equally represented in the outcrops and quarries (Figure 5a), having hipidiotopic to xenotopic macrocrystalline texture, often accompanied with brecciated dolomite fabric (Figure 5b). These are, again, rocks with a significant secondary porosity of

the diagenetic origin in light-colored crystalline dolomites, further enhanced, due to the tectonics, in dolomite breccias. All these carbonate rocks described in the Medvednica mountains are intensively weathered and karstified at the surface outcrops, and they represent significant and valuable volumes for karst aquifers development. This is also acknowledged for the similar Triassic carbonate rocks from the Papuk mountains [25].

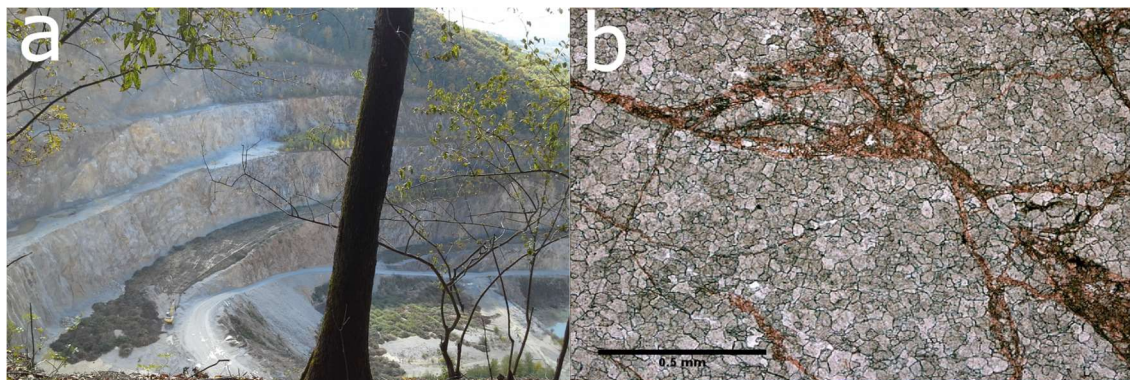


Figure 5. (a) Outcrop with light gray dolomite in the Medvednica mountains (Ivanec Quarry); (b) Photomicrograph of the brecciated light gray dolomite (The width of the microphotograph is 1.7 mm).

Low-grade metamorphic rocks of the greenschists metamorphic facies from the central part of the Medvednica mountains [16] represent an analog for similar metamorphic rocks in the pre-Neogene basement of the CPBS. These rocks are the products of low-grade metamorphism, affecting the Mesozoic older sedimentary and volcano–sedimentary successions [20,26,27]. Their appearance at outcrops (Figure 6a), as well as in the hand samples (Figure 6b) shows compact, lepidoblastic and nematoblastic schist structures.

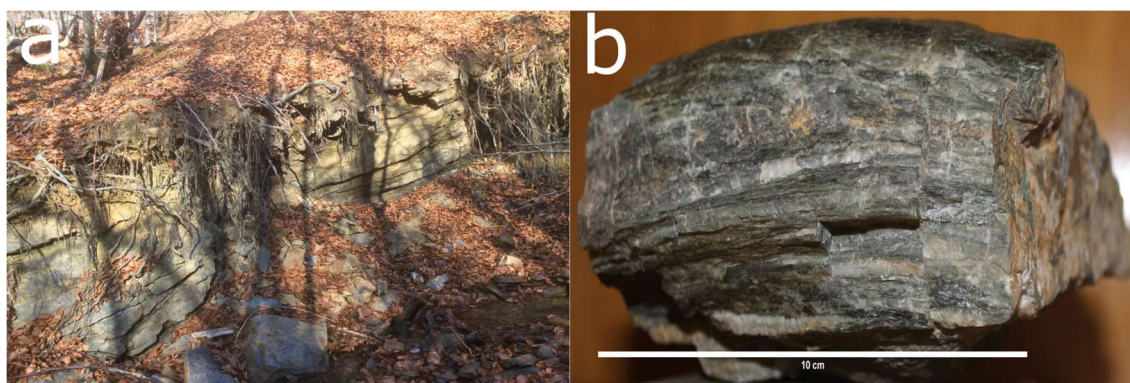


Figure 6. (a) Outcrop with the greenschists in the Medvednica mountains; (b) hand sample of the greenschist from the Medvednica mountains.

Physical properties of greenschists often show anisotropy due to their structure and their porosity is lower than in observed sedimentary carbonate rocks, unless the rocks are later tectonized and secondary porosity of tectonic origin developed as cracks and fissures within the rocks.

Magmatic rocks occasionally intruded within the other pre-Neogene basement rocks of the CPBS. Recently, several types of granitoids from the pre-Neogene basement of the CPBS were reported from the deep wells in Eastern Croatia. These rocks were analyzed and interpreted as shallow plutonic alkali–feldspar granites; hypabyssal monzodiorites–granodiorites; as well as monzogranites and leucogranites [28]. All these rocks are more-or-less compact and they have grainy to porphyric

structures with low porosities, unless they are later tectonized, similar to the previously described metamorphic rocks.

3. Basic Geological Settings of the Pre-Neogene Basement Rock in the Northern Croatia

All rock types drilled and discovered in northern Croatia could be divided in two different groups. The first, younger group, includes Neogene and Quaternary deposits and the second group the rocks in the pre-Neogene basement. They are also lithologically very distinctive. The Ng–Q sediments are clastics and basement rocks are carbonates (mostly Mesozoic), as well as magmatites and metamorphites (mostly Paleozoic). The younger group is better explored, but enough regional data are available for both groups. The Mz–Pz group was marked as a target for subsurface disposal of wasted nuclear fuels, i.e., radioactive waste, because of: (a) depth, (b) compactness and hardness with lower porosity and permeability, (c) lower influence of neotectonic displacements, (d) they are not subdued to meteoric, but only connate waters.

The entire northern Croatia is a part of the CPBS, shown on Figure 7, divided in the four large, regional depositional–tectonic structural units of the 2nd order. Those are Mura, Drava, Sava and Slavonija–Srijem Depression. In the Sava Depression two regional units of the 3rd order are located—the Karlovac and Požega Subdepression and in the Drava Depression—the Bjelovar Subdepression. The basement rocks are explored on the hills and mountains at margins (e.g., Trgovska gora Hill) and in central parts (Medvednica, Moslavačka gora, Psunj, Papuk, Požeška gora mountains).

The CPBS (e.g., [1,29–34]) was created at the margin of the Pannonian Basin System (PBS), which resulted in some depositional and tectonic specific features. The entire CPBS is created along the several regional transcurrent faults. The first lake environments were created in the Lower Miocene. During the Lower Badenian (16.4–15.0 Ma), the 1st marine transgression of the Central Paratethys covered the northern Croatia, overlying the siliciclastic basement with dominant alluvial fan deposits and corallgal bioconstructions deposited during the fast subsidence (1st transtensional phase). During the Middle and Upper Badenian (15.0–13.0 Ma), tectonics was weak and fine-grained clastics and carbonates were deposited. The period ended with the 2nd flooding of the Paratethys.

It was followed with the 1st transpressional phase from the Sarmatian to the end of the Lower Pannonian (13.0–9.3 Ma), when the Pannonian Lake (brackish to freshwater) was gradually created. Then followed by the 2nd transtensional stage, which lasted throughout the Upper Pannonian (9.3–7.1 Ma) and Lower Pontian (7.1–6.3 Ma). The monotonous, thick marl and sandstone sequences were deposited, first in the Pannonian Lake, later in local Sava and Drava lakes. Sandstone detritus originated from the Eastern Alps, transported by turbidites and redeposited on tectonic ramps. Marls are typically of lacustrine origin.

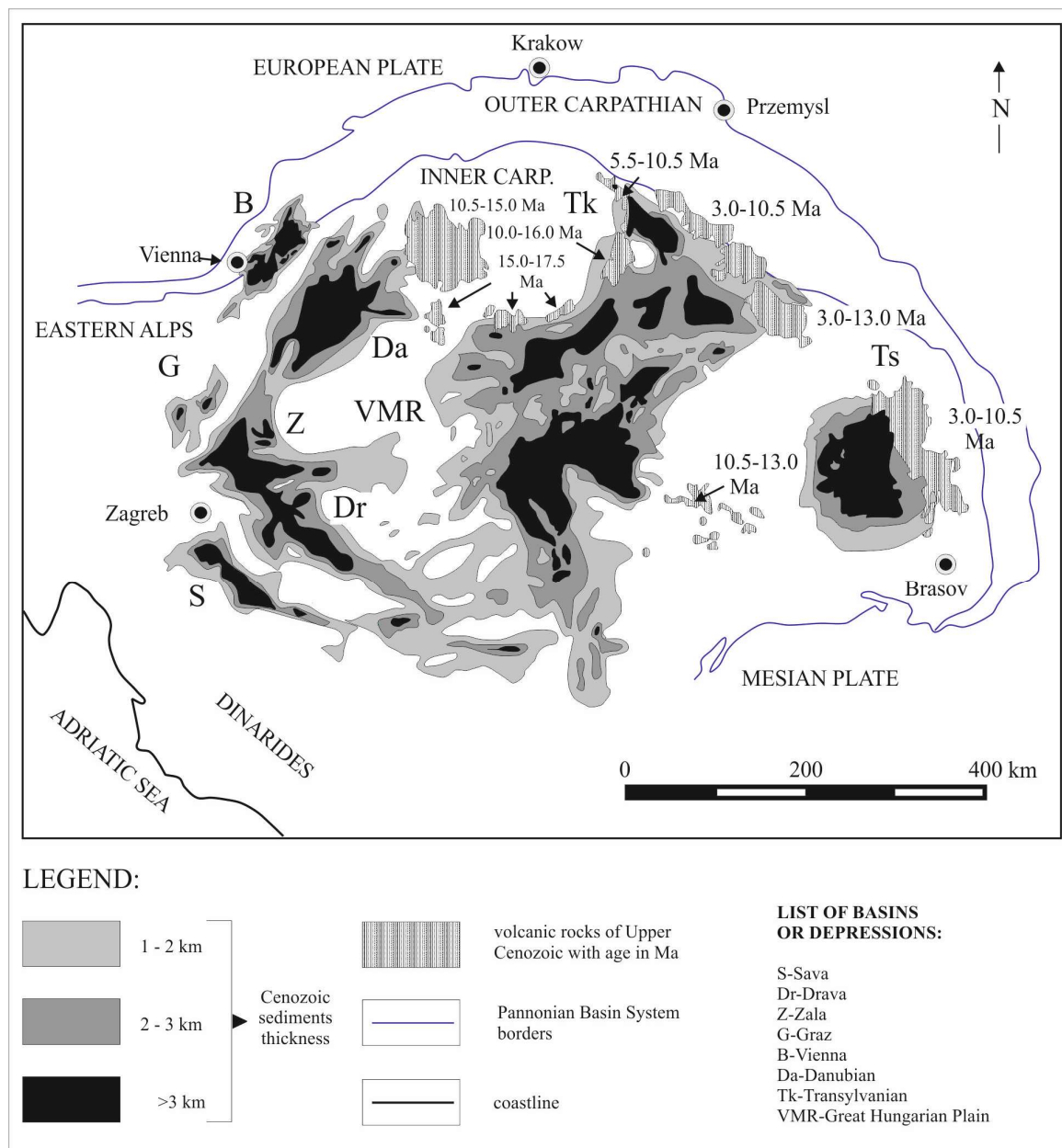


Figure 7. Location of the Croatian part within the Pannonian basin system/CPBS in the PBS [1].

The last, 2nd transpressional phase, started in the Upper Pontian (6.3–5.6 Ma). The lacustrine environments are reduced to the Slavonia Lake, eventually closed in the Pliocene (5.6–2.6 Ma). The Quaternary (2.6–rec. Ma) is characterized by a completely continental environment. During the entire Upper Cenozoic, especially during the transpression, older structural highs and mountains (e.g., Medvednica, Papuk, Psunj mountains) were uplifted, including the youngest Bilogora mountains, completely uplifted during the last 2.5 Ma [35]. It resulted in a significant thickness of the Ng–Q sediments with more than 7000 m in the Drava and more than 5000 m in the Sava Depression. Depositional evolution and lithology of the CPBS are clearly visible in regional lithostratigraphy and can be easily correlated and compared in all depressions (Figures 8 and 9).

The long-lasting deposition and tectonics resulted on numerous structures and fault zones. The major ones are mapped from the basement up to surface, other are local and shorter. However, along the major fault systems, throws could reach several hundred meters (Table 1, locations are

given at Figure 10), as observed on examples taken from the regional structural map of the Bjelovar Subdepression [37].

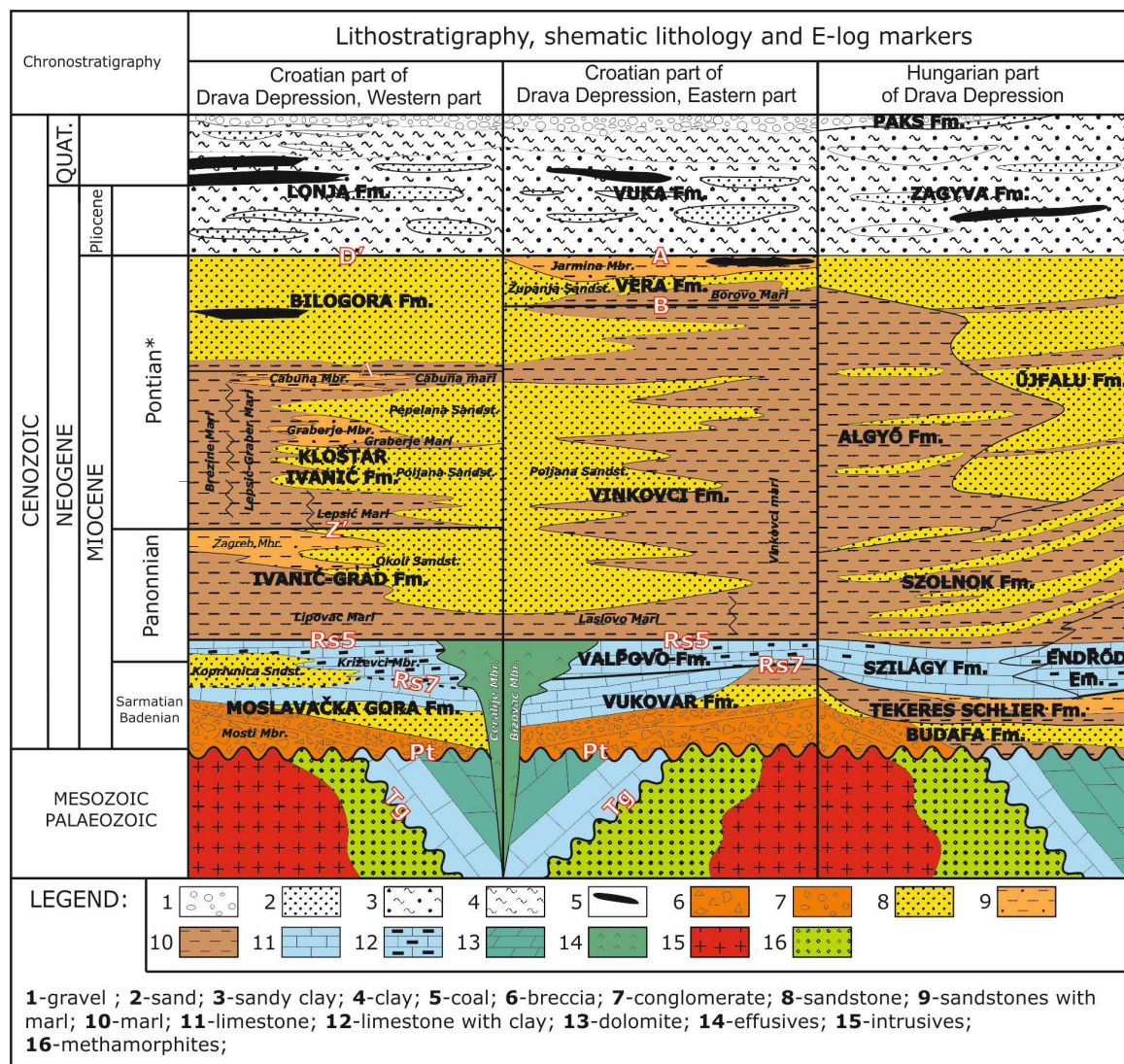


Figure 8. Schematic lithostratigraphic columns of the Drava Depression [36].

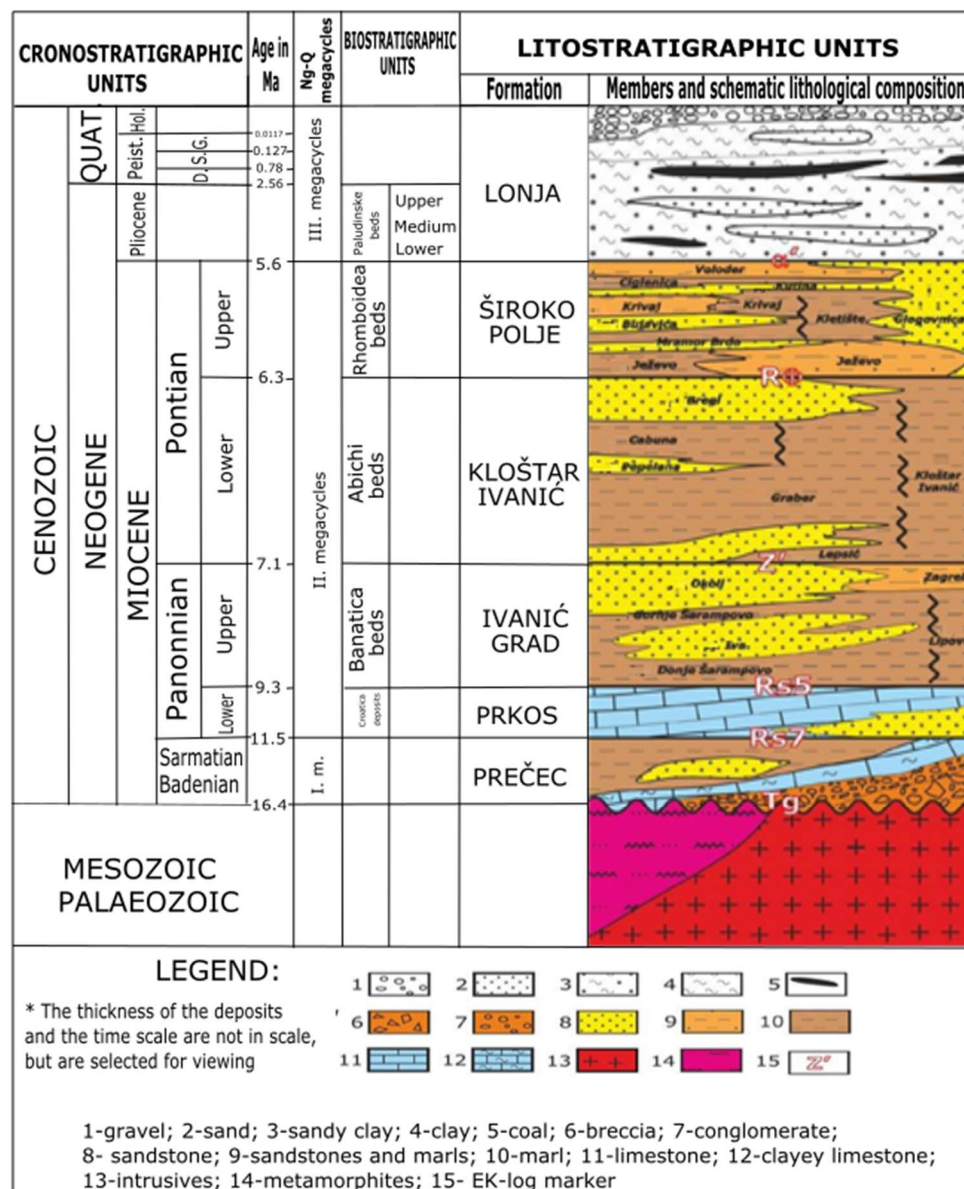


Figure 9. Schematic lithostratigraphic review through the Drava Depression [8].

Table 1. Absolute vertical fault throws (in meters) along the main fault zone in the Bjelovar Subdepression [37].

	Pre-Cenozoic– Miocene (16.4 Ma)	Sarmatian–Early Pannonian (11.5 Ma)	Early–Late Pannonian (9.3 Ma)	Late Pannonian–Early Pontian (7.1 Ma)	Early–Late Pontian (6.3 Ma)	Late Pontian–Pliocene (5.6 Ma)
Transverse Normal Faults (NE–SW)						
(1) Primary normal	300	100	100–200	100	100	50
(2) Secondary normal	100	100	100	–	–	–
(3) Western	150	100	100	50	50	50
(4) Štefanje	50	50	50	50	50	50
(5) Eastern Marginal	100	100	Unconformity	Unconformity	100	50
(6) Uljanik	100	100	Unconformity	Unconformity	100	50–100
Diagonal Faults (WNW–ESE)						
(7) Bilogora	200	100	100–200	100	50	100
(8) Šandrovac-Ciglena	50	100	100–200	50	50	50
(9) Primary reverse	200	100	100	100	100	50
(10) Secondary reverse	200	100	50–100	100	–	–

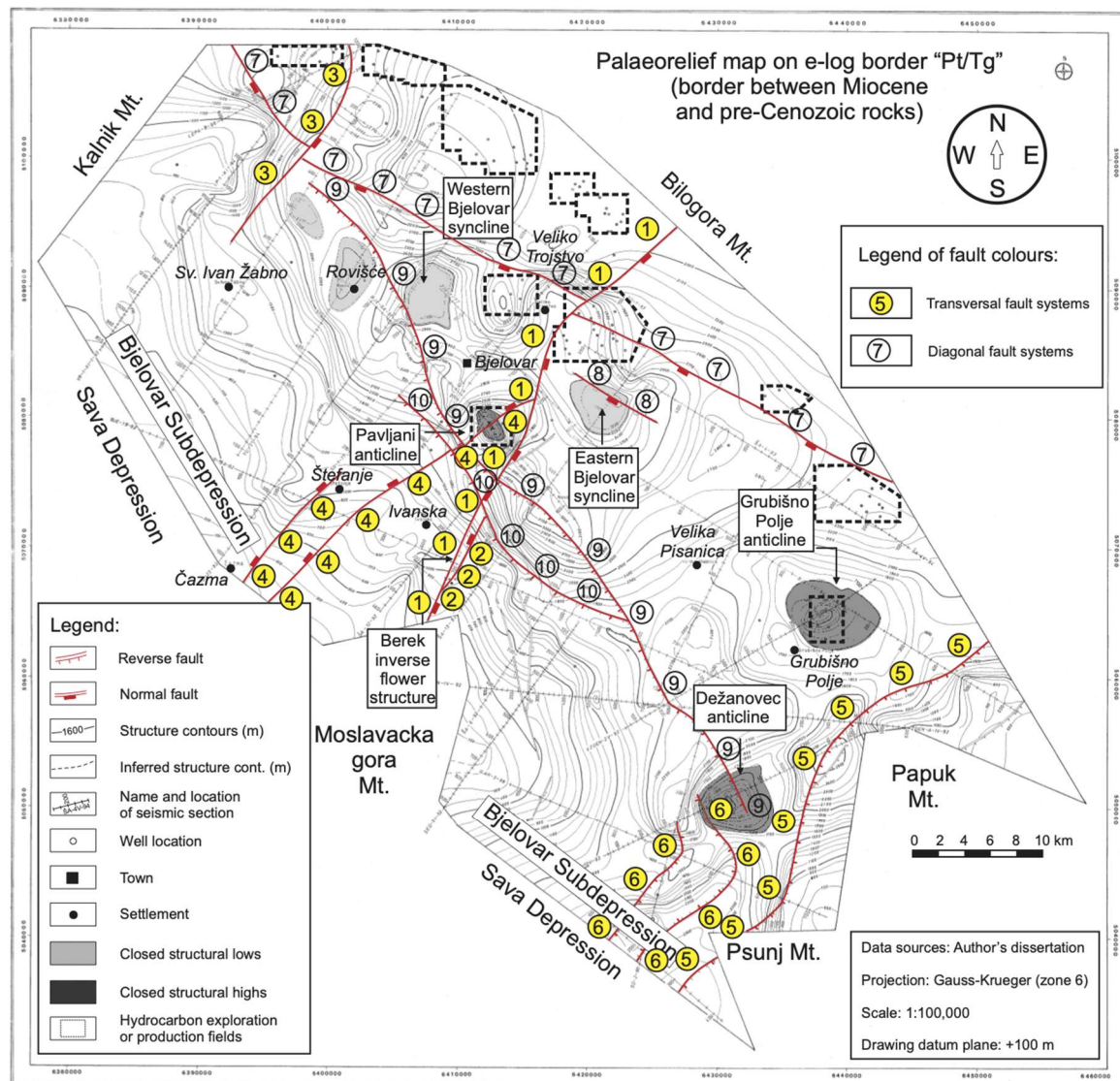


Figure 10. The main fault zones in the Bjelovar Subdepression shown on paleorelief map of the Neogene basement [37].

4. Lithology and Petrophysics of the Pre-Neogene Basement Rock in the Northern Croatia

As mentioned, there are two lithological types of the Neogene basement: magmatics and metamorphics, dominantly Paleozoic and carbonates, mostly Mesozoic.

Magmatics and metamorphites are, in practice, named as "Basement Rocks" (Croat. "temeljno gorje"). Such name can also be considered as an informal lithostratigraphic unit of a group rang. Paleozoic is often composed of granites and gabbro intrusions, and, by intrusion, cracked and altered, metamorphized rocks. Metamorphites include the rocks of the amphibolitic facies with different schists and gneisses.

In addition, they were subdued to several orogeny cycles and displaced from their locations numerous times. However, deep data can be correlated with the same lithotypes collected from outcrops on mountains and hills in the CPBS. Dominantly, those rocks are of the Paleozoic, but some are of the Mesozoic age. For example, Pandžić [38] stated that ophiolites in the SW part of the PBS were continuously created both in Paleozoic and Mesozoic. Later, Hertz [39] assigned the gabbro and serpentinite on NW Majeveca and Trebovac to the Upper Cretaceous. The most of the schists were formed during the intrusions of granite magma, caused by the contact metamorphosis, resulting in quartz–mica and quartz–mica–chlorite schists. Mineral paragenesis indicates the greenschist facies.

Well data are extremely significant for the determination of petrophysical values, particularly in the weathering zone, which is almost always developed in the topmost part, also characterized with secondary porosity. Such weathering mostly happened during the Paleogene and could develop from several meters to several dozens of meters from the basement top.

The next group of carbonate rocks was named in practice as “Tertiary basement” (Croat. “podloga tercijsara”; today Paleogene and Neogene Basement should be used instead of the Tertiary) and can also be considered as an informal lithostratigraphic group. Those are different limestones and dolomites, often cataclyzed and weathered in breccia and conglomerates, especially in the youngest part. Such rocks are also drilled in the deepest parts of the CPBS, such as in the Drava Depression in the wells Vir-3 (where effusives are syngenetic with carbonates) and Or-1 (Figure 11) where dolomites are detected at −4740 m.

Petrophysical values of the basement rocks are mostly very rare, when compared with younger rocks in the CPBS. However, the dataset was comprehensive enough to get a regional insight in interval values of porosity and permeability, as critical variables for any estimation of sealing properties, which can be calculated from cores or logs. Such values were generally low, lower in the magmatic–metamorphic than in the carbonate basement (with much stronger influence to dissolving and cataclysing). In basement, for example in the Bjelovar Subdepression, porosity varies between 0.9% and 4.1% in different schists, quartzite sandstones and gabbro. The maximal vertical permeability is, in VT-1 well, $0.24 \times 10^{-3} \mu\text{m}^2$. The basement rocks, as well as hydrocarbon reservoirs in them, can be easily recognized on e-logs (Figure 12). This is an example of how e-log allows to recognize metamorphic basement (not a discussion about hydrocarbon reservoir existence). In addition, the existence of reservoirs does not mean that “seal” is not appropriate for nuclear waste disposal. If migration happened several Ma ago, it could be considered an appropriate safe medium for waste disposal.

In Mesozoic carbonates, the petrophysical values were generally slightly higher, e.g., 2%, with both permeabilities mostly less than $0.1 \times 10^{-3} \mu\text{m}^2$ (example of Dež-1 well, Bjelovar Subdepression).

There were also interesting data about the basement saturated water salinity. As average for the Drava depression, Cota & Britvić [42] referred 18 g/L NaCl for magmatites and metamorphites and 15 g/L for carbonates. However, locally, values can significantly vary [43], from 3.24 (Gr-1z) to 15.34 g/L (Pav-1) for magmatites/metamorphites and from 9.9 (VC-1) to 23.29 (Ptk-1) g/L. The lower values in magmatites/metamorphites are the probable result of mixing with waters from younger formations and higher in carbonates with longer inactivity of the aquifer and consequently more strongly dissolved.

There is also one very famous structure in the CPBS where Paleozoic and Mesozoic rocks can be simultaneously studied, based on numerous data from deep wells, seismic and logs. That is the Molve Structure, located in the central Drava Depression (Figure 13).

The Molve structure is particularly interesting because hydrocarbon reservoir included four different lithofacies, from the Paleozoic to the Badenian (Middle Miocene), each with its own petrophysical properties, but still representing a single hydrodynamic unit. Those four lithofacies (e.g., [44]), range from pre-Devonian to the Middle Miocene and from the granite and amphibolitic schists, metasandstones, quartzites, carbonates to the lithothamnion limestones, biocalcarenes and biocalcrudites.

Analyzing the porosity variations through those four lithofacies, it could easily be observed a regular decreasing of values along the depth and age of rocks (Figure 14). It goes from 20% in the Badenian breccia, to less than 2% in Paleozoic diaphthorite rocks. However, some samples from diaphthorite rocks develop secondary porosity around 20%, which is a clear indication of strong weathering zone in the topmost part of the basement.

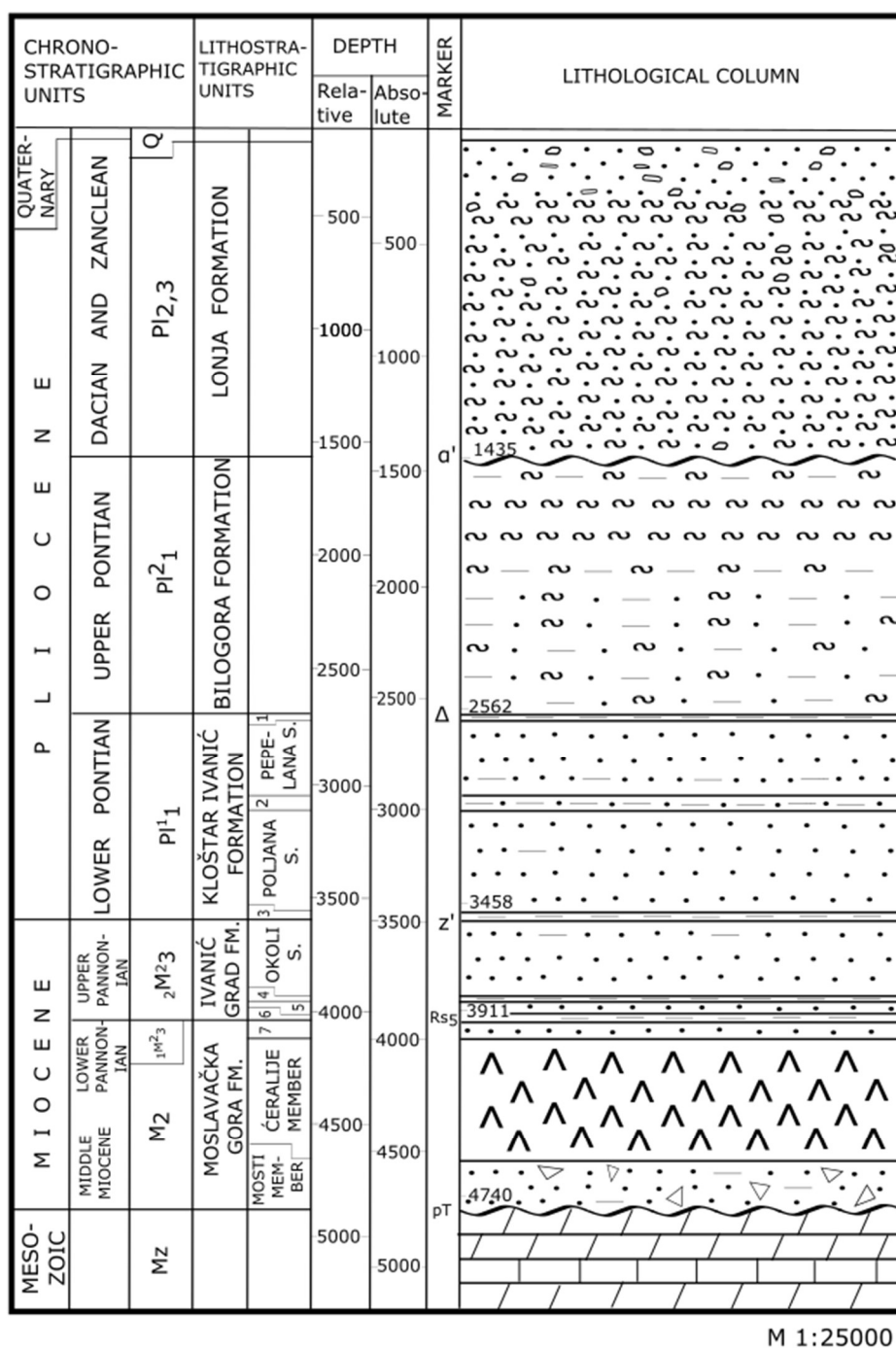


Figure 11. Lithostratigraphic section in the well Or-1 (original redrawn from [40]). Numbers in legend mark thin members.

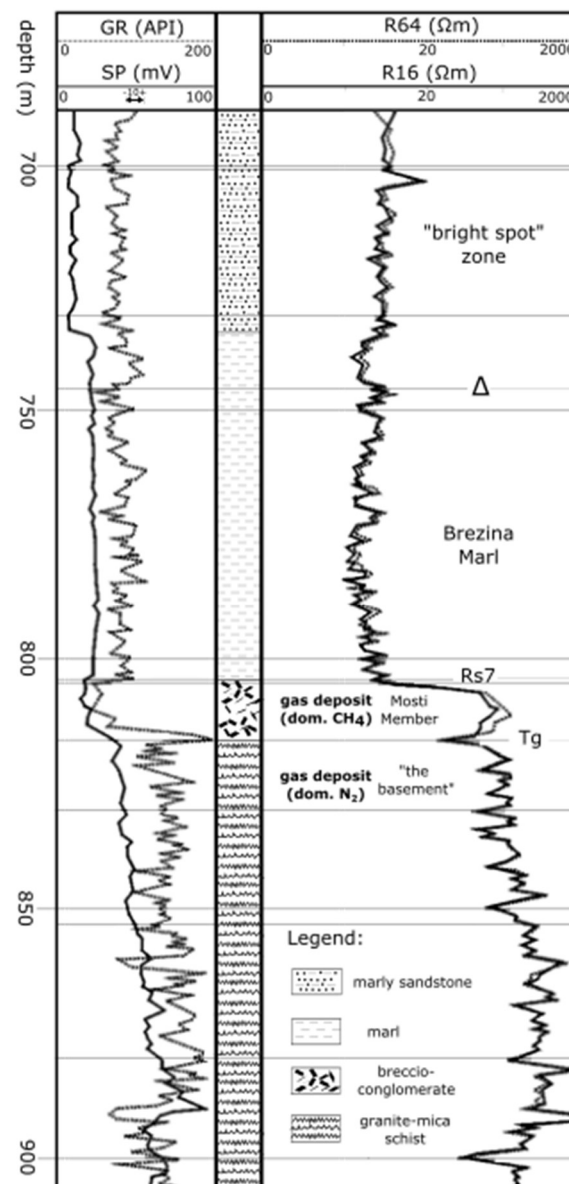


Figure 12. Conventional log in the Paleozoic basement rocks, well Gr-1z, eastern Bjelovar Subdepression (original redrawn from [1,41]).

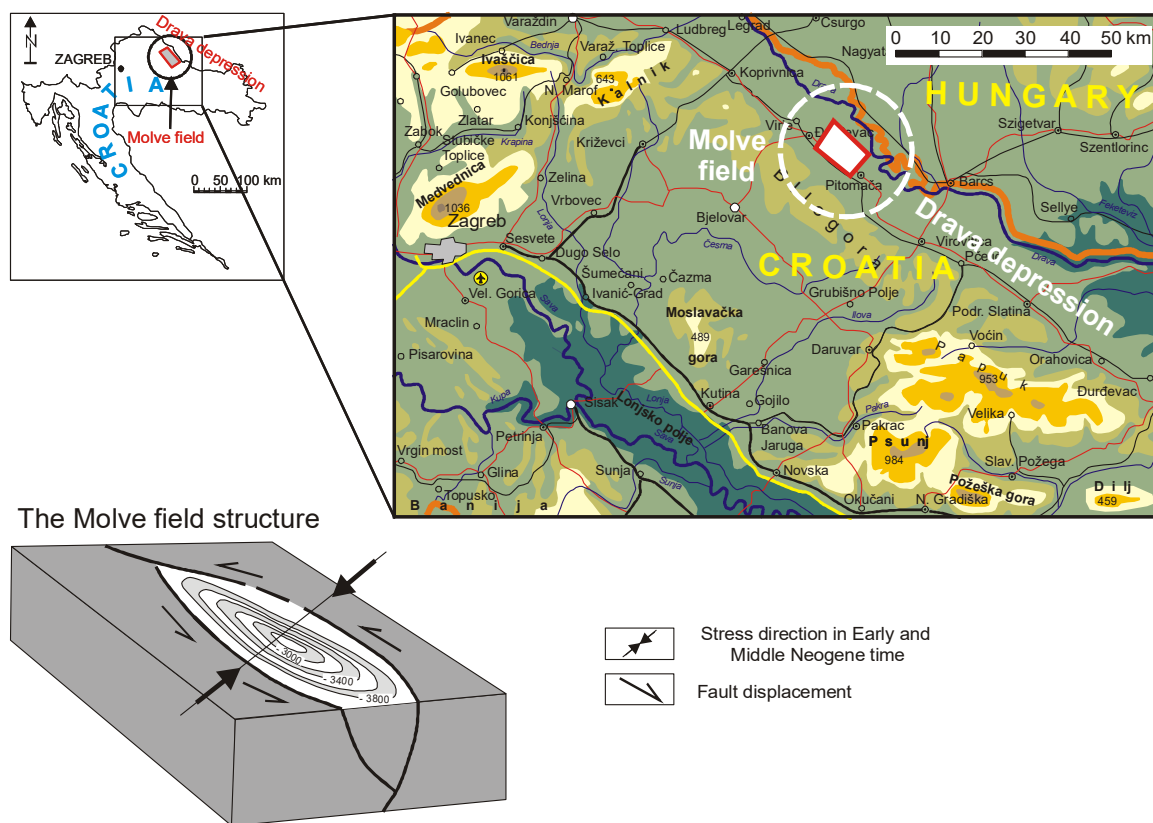


Figure 13. Geographical location of the Molve structure [44].

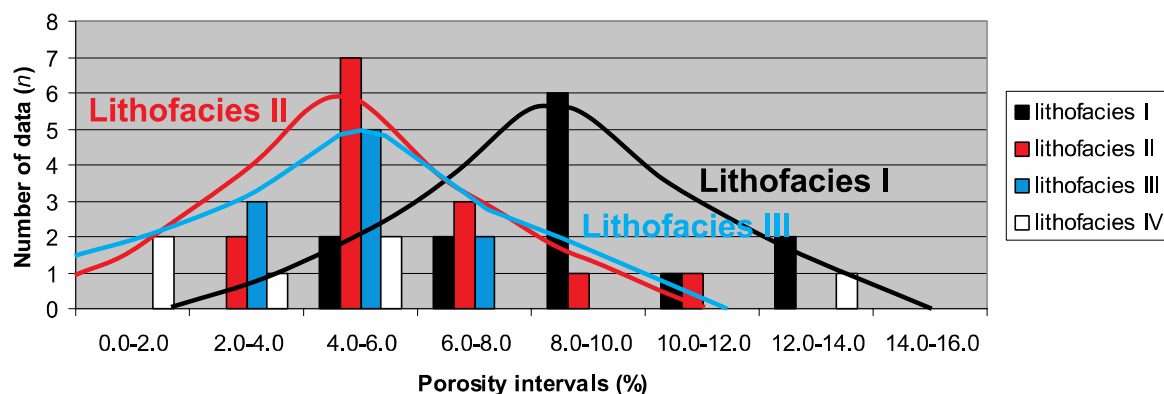


Figure 14. Histograms of interval porosity values in the lithofacies of the Molve structure. The lithofacies I-III could be approximated by the Gaussian distribution [44].

5. Proposal and Discussion of a Modified PoS Methodology for Radioactive Waste Disposal in Pre-Neogene Basement of the Northern Croatia

Every modeling in the subsurface exploration can comprise two main routines: static geological modeling and dynamic engineering simulation. Both can be done simultaneously or only the static model can be applied during the early, exploration phase. These two approaches are often interconnected in one general integrated model. A complete geological model includes numerous analytical methods (stratigraphic, structural, tectonics studies, petrophysical and geochemical variables analyses, creation of maps). In a later stage, fluid migration parameters could be also collected. All or most of these data need to be collected during the modeling of deep borehole disposal (DBD) radioactive waste program.

For any variable, the most important property is a spatial continuity, which is directly connected with data quantity and clustering. The geological variables (e.g., porosity, permeability, thickness) have spatial continuity, which could be expressed via autocorrelation function (such as a variogram). They are also regionalized variables with known general statistics, but also with an uncertainty interval. This has to be taken into consideration when these variables are selected in the modified PoS intended for DBD of highly radioactive waste (HLW). Previously, two assumptions are set for the selection of favorable geological units for HLW disposal: (1) promising structures are selected on structural and paleostructural maps; (2) promising lithostratigraphic units are selected in basement with low petrophysical values.

5.1. Connections between Categories in Classical and Modified PoS Models (Hydrocarbon vs. DBD Critical Variables)

The PoS table used for hydrocarbon reservoir probabilities is largely modified, using only two assumptions. The classical principle, based on the workflow published, e.g., in White [45] and Hernitz et al. [46] studies, was carefully redesigned for each of the basic categories defined in a typical hydrocarbon system. Similar modifications have been done in the past, but to a lesser extent and for problems still defined in hydrocarbon systems. Example of such PoS systems, applied in the CPBS, can be found in Malvić & Rusan [3,47] studies. However, the basement rocks in northern Croatian subsurface are not still extensively explored, so no modified PoS methodology intended to assess the HLW based on different geological variables can incorporate a detailed list of numerous geological events and probabilities. Consequently, most variables in categories of hydrocarbon systems must be replaced or omitted.

Category “Source rocks–maturity–migration”—The existence of source rocks is not important for the assessment of basement rocks, particularly because they cannot contain source facies at all. In addition, the role of migration in hydrocarbon systems is crucial, but in HLW it is the most unfavorable event. For that reason, it was omitted in the modified PoS. However, the temperature variable, as a crucial parameter for organic matter maturity, is important for the long-term preservation of any artificial inputs in basement rocks in “original” or intact state. Hence, the variable “temperature” was inserted in the modified PoS as a new category.

Category “Trap–isolator rocks–time”—Trap is a variable which does not exist in the HLW systems in the connotation of hydrocarbon reservoirs, because solid waste is disposed in the rock systems where neither structural closure nor migration time is important. The sealing properties are the only and the most important variables. That has to fit the condition that any migration of radioactive nuclides must be stopped and practically slowed to zero regarding the geological time scale. Hence, in this particular PoS modification, the isolator properties (natural and artificial) need to be highlighted as a category.

Category “Reservoir–porosity–permeability”—Reservoir rocks are one of the most critical parameters. In hydrocarbon system it is the most favorable and in the DBD the most disadvantage variable. Any type of porosity (either primary or secondary) and permeability are not desired in the DBD program and are considered as a critical variable for the new category. The fault zones, as the second critical variable, also decrease the permeability of DBD volume for HLW, in particular such fault zones where cementation has not happened or finished.

Category “Preservation–quality–producing”—This category is almost entirely very specific for hydrocarbon systems. Preservation, production and quality of hydrocarbons are not connected in any way with the HLW, except as indicators of subsurface fluid activity, causing flushing, degradation or ionic exchanges. Most such events are a result of regional stress, salinity stratifications and regional hydrological conductivities. Hence, the aquifers’ properties would be presented as a category, connected with numerous measurements from the previous ones.

As in hydrocarbon systems, the DBD of radioactive waste is based mostly on measurements from deep wells. Improvements in drilling technologies in the past revived the DBD for disposal of HLW, like SPN and plutonium, instead of the placement in underground mines, e.g., at depths 500–800 m

(e.g., [48]). The large-diameter cased boreholes (e.g., for the lowermost interval, it could be 0.194 m for drill pipe, 0.305 m for drill collars and 0.356 m for drilling [48]) can be used at 4–6 km depths, to safely dispose the HLW into the granitic basement, i.e., upper part of the continental crust. The radioactive waste is disposed below drilled sealings [48]. The granite is almost always considered as an ideal lithology for HLW disposal all over the world. For example, Wang [49] described the Beishan area (NW China, Gansu Province) as the most suitable country area for HLW repository because of its favorable socioeconomical and natural conditions, which included eight (3 the most) favorable granite intrusions, where total crust thickness 47–50 km and no earthquakes with $M_s > 4.75$ were recorded. The hydraulic conductivity ranges between 6.6×10^{-10} m/s and 3.9×10^{-14} m/s [49]. Considering also the moderate in situ stress (4.54–12.77 MPa), the described granite could be a location for the permanent disposal of HLW. However, such sites are sensitive to the complex stress fields, which could initiate earthquakes. Their triggering is related to changes in stress fields [50]. Consequently, it is necessary to make a map of earthquake distribution in the analyzed area and point out all of them with some “critical” magnitude (e.g., $M_s > \text{five or six}$), which happened in the past and are recorded in historical data.

5.2. The New Categories and Critical Variables

The categories and parameters for the modified PoS which could be applied for radioactive waste disposal (critical variables are included) in northern Croatia are shown in Table 2. All probabilities can range between 0.0 and 1.0. A value of 1.0 is added if all subcategory criteria are completely satisfied at the most favorable level. Oppositely, if none of such criteria is matched, the value is 0.05 (if measurements are missing) or 0.0 (if non-existence is proven). Single category 0.0 value makes all further calculation unnecessary (e.g., [4,5]).

The probability values are connected with the original PoS applied for hydrocarbon reservoirs in Croatia and simply define statistical quartiles. Such approach proved to be successful in the assessment of both potential and proven reservoirs, just as simple and comparable with other reserves classification, qualitatively described as possible, probable and proven. With the present level and quantity of the northern Croatian basement data, it is reasonable and logic to continue to use such probability quartiles in an exploration phase, until the new data and benchmarking reveal the necessity to define more probability classes, maybe even of irregular probability intervals. A special attention must be given to the selection between probabilities 0.05 and 0.0. While the last one makes the calculation meaningless and does not require new data, the value 0.05 oppositely and inevitably needs collecting new data because the variable cannot be estimated due to insufficient measurements. In both cases, the total probability will be significantly smaller than 1.0, which could result in the elimination for any structure where safety needs to be 100%. Consequently, expert analysis is necessary.

A. Temperature. As one of the critical variables, temperature can degrade the stability of any metal or concrete container-based protection during a long-time interval (10^2 – 10^4 years). Cumulative temperatures in the disposal volume could be the result of several sources. The natural sources are heat flow or geothermal gradient and the heat released from radioactive decay. The source could be induced energy released from the heaters used to melt and recrystallize the rock where containers are disposed.

In addition, sealing properties depend on the temperature. For example, Gibb et al. [51] proposed using high-density support matrix (HDSM) for sealing of waste which, while decaying, generates temperatures higher than approximately 185 °C in the annulus (volume between the disposed package and borehole walls). If the basement rock temperatures could be expected to reach 80–130 °C [48], it is obvious that the decay will generate additional heat, especially if highly radioactive fuels had not undergone the process of cooling. The question is if such additional heat will lead to an increase in the temperature that will alter the host rock and the waste containers. As a possible solution to such problem, the HDSM includes lead-based, fine-grained, alloy that is delivered after each waste package [51], filling all pores around such containers, in an uncemented zone, i.e., between casing and walls.

Table 2. Categories and variables selected for the modified PoS to potentially be applied for radioactive waste disposal in northern Croatia.

Categories and Variables	Probabilities for Particular Structure in the Croatian Part of the Pannonian Basin System (CPBS)	
	Probability of the Crucial Geological or Engineering Events in the Category (0–1)	Probability for Category
(A) temperature		
<i>a1.</i> The present-day temperature in basement rocks is considered as a long-term value.	$a1 \times a2 \times a3 \times a4 =$	<i>A</i>
<i>a2.</i> Quaternary volcanism is not observed.		
<i>a3.</i> The paleothermal gradient is known at least for the last 100 Ky.		
<i>a4.</i> Heat flux <75 mW/m ²		
(B) sealing properties of rock		
<i>b1.</i> Lithological isolator properties need to be proven all around the disposal volume.	$b1 \times b2 \times b3 \times b4 =$	<i>B</i>
<i>b2.</i> Granite is favorable, magmatic and metamorphic rock types are a necessary condition.		
<i>b3.</i> The sedimentary sequence in the top of granite/magmatics is rich in clayey and fine-grained rocks (claystones, marls ...).		
<i>b4.</i> If artificial sealing of the borehole displacement zone is performed, its quality must be proven.		
(C) low petrophysical values + fault zone(s) inactivity		
<i>c1.</i> Petrophysical properties (<2%, <10 ⁻¹⁵ m ²) needs to be proven in the entire volume.	$c1 \times c2 \times c3 \times c4 =$	<i>C</i>
<i>c2.</i> Fault zone(s) must be inactive or with throw less than 50 m in the Quaternary.		
<i>c3.</i> Regional fault zones must be located more than 2 km from the disposal, and the closest fault zone(s) must be cemented.		
<i>c4.</i> Depth of HLW disposal has to be more than 3 km.		
(D) subsurface fluids and aquifers		
<i>d1.</i> Subsurface fluids and aquifers must be regionally still, i.e., inactive.	$d1 \times d2 \times d3 =$	<i>D</i>
<i>d2.</i> The deep saline aquifers are favorable.		
<i>d3.</i> Regional weathering zones must be absent or separated from the disposal, with enough thick sealing part of basement.		
STRUCTURE PROBABILITY (<i>E</i> = <i>A</i> × <i>B</i> × <i>C</i> × <i>D</i>)		<i>E</i>

The strongest natural influence on subsurface temperature comes from the geothermal gradient, i.e., geothermal heat flux, regional as well as local. In Table 3, a heat flux of the upper marginal allowed value <75 mW × m² for the DBD, is proposed. The regional mean value calculated for the CPBS is 76 mW/m, with geothermal gradient ranging approximately 0.04–0.07 °C/m [52,53]. For the higher interval value of gradient, the temperatures at the depths of three or more km could be higher than 200 °C and special attention needs to be given on the stability of casing and containers.

B. Sealing properties of rocks. Sealing rocks have to be located all around the disposed containers. Franklin et al. [54] mentioned that DBD would be ideally at 3–5 km (or at least >2 km, where overlying argillaceous rocks could be beneficial) in crystalline basement, reaching robust geological conditions that demand the minimal engineering support.

Sealing properties need to be assessed both through basement lithologies as well as artificial sealings. Major uncertainties exist regarding the length of time that has to be guaranteed for the disposed materials inactivity. The quality of filling has the largest influence in case of drilling the

damage zone (or excavation damage zone (EDZ)). Such zone, in granite, could be restricted to a few tens of centimeters [48]. According to Gibb et al. [56], EDZ thickness at mining enterprises during the usage of “conventional” technology varies between 0.3–1.4 m

Table 3. Examples of technical criteria for selecting a potential site for consideration, which would contribute to the safety case (taken from Franklin et al. [54]; which modified it from U.S. Nuclear waste technical review board [55] and U.S. Department of Energy (DOE) documents).

Characteristics	Criteria
Depth to crystalline basement	<2 km
Simple basement structure	No known regional structures, major shear zones, major tectonic features within 50 km
Low seismic and tectonic activity	No Quaternary age volcanism or faulting within 10 km
Absent flow of fresh groundwater at depth	Absent significant topographic relief to drive deep recharge, old and highly saline groundwater at depth
Low geothermal heat flux preferred	<75 mW/m ²
Sufficient area for well array	Design-dependent
Absent existing contamination	Absent surface or subsurface contamination at the proposed site
Minimal disturbances from other surface or subsurface uses	Prefer sites with minor impacts, e.g., wastewater injection, oil and gas activities, groundwater production, mining and potential mineral resources in the bedrock

The EDZ, as a bypass, must be eliminated at least locally, i.e., in intervals just above the disposal zone. One of the methods [51,57,58] similar to HDMS, could be applied at the selected borehole interval where casing is removed and finely grained, crushed granite (or any host rock) is backfilled. Such detritus is partially melted together with host rock using the artificial electrical heating and left to slowly cool and recrystallize into the virtually original host rock, but without borehole damaging zone. The process is known as rock welding (e.g., [48]), where partial granite melting happened at 700–800 °C, and then cooling, finishing recrystallization at about 550 °C. Eventually, natural and artificial sealing properties create stable DBD volume.

C. Low petrophysical values + fault zone(s) inactivity. Based on experimental values from the explored cores in the CPBS, the basement structures are often characterized with porosities less than 2% and accompanied with less than 10^{-15} m² permeabilities (both in vertical and horizontal directions). In crystalline basement depths of a few kilometers, such values could be expected. For example, Beswick et al. [48] reported for such rocks very low bulk hydraulic conductivities ($\leq 10^{-11}$ m/s), even in fractured parts and saline brines, which do not mix with meteoric groundwater (rarely extending below 1–2 km), making density stratification. As a result, HLW cannot move far away from the disposal place. Generally, crystalline rocks, especially in the stable mid-continent region, can be low permeable, where permeability of unfractured crystalline bedrock ranges from 10^{-16} m² to 10^{-20} m² [59]. Values decline with depth due to the increasing confining pressures [48].

Fault zones must not cross disposal volumes and the closest ones must be inactive. The fault zone inactivity is hard to estimate. It depends on numerous parameters like periodicity of fault activity, size of the fault zone, length of fault, age of fault, cementation of the fault zone, etc. In Table 3 it is indicated that disposal place needs to be more than 10 km of active regional fault zone. However, as the CPBS is much narrower than the mid-continent plateaus, and the deepest parts are connected with fractures along the main regional fault zones (Table 1, Figure 10), the 10-km limits would eliminate much of the deep basement as a target for the disposal. Respecting the regional paleorelief maps and hydrodynamics in discovered hydrocarbon reservoirs, the minimal two-kilometer distance between DBD well and main depressional fault zone was set. Such reservoirs exist at least unchanged in upper Quaternary, representing more than one million years ago. Without further drilling and benchmarking, this value cannot be precisely defined, and it cannot be assessed with probability 1.0, but rather with 0.5 or so.

As an elimination parameter, the Quaternary volcanism (Table 3) does not need to be applied in the CPBS (no present-day volcanic activity of shallow magma chambers), but fault activity does. The Quaternary inactivity (and Neogene low activity) of regionally fault zones is a necessary condition in the selection of the DBD zone. Based on the regional palinspastic analysis (e.g., Table 1) low fault activity could be described, Quaternary cumulative throw up to 50 m, but inactive faults would not have any throw at all to fulfil probability of 1.0 as safe critical variable.

D. Subsurface fluids and aquifers. They have to be still, regionally inactive, where the pressure gradient is gradually dispersed through rocks, mostly with geostatic normal pressure. “Safe and slow” flow would occur in nanosized pores found along the edges of crystals (e.g., [54]), not through the developed fracture systems, when basement crystalline rocks may have much higher permeabilities in connected natural fractures. Nevertheless, there will be upward transport of radionuclides due to the presence of hot waste, sometimes supported with secondary permeability from drilling damage and leaky sealing materials. Moreover, radioactive heating can pressurize the connate water around the boreholes and create the initial potential for fluid flow, and buoyant thermal convection will maintain flows over longer times (e.g., [54]), such as the gases developed by the decomposition of the waste containers. Weathering zones could be a crucial unfavorable factor in the CPBS due to the geological history. During the entire Paleogene, most basement surfaces were largely exposed in continental facies subdued to strong weathering and developed thick breccious lithofacies (e.g., [30,31]). Such lithology, if not cemented later, enabled the strong and continuous migration during the long geological time, even until the Quaternary (when hydrocarbon migration happened in the CPBS). That is proved by numerous discovered hydrocarbon reservoirs where oil and gas are found in single hydrodynamic units, simultaneously encompassing pre-Neogene basement and the Badenian coarse-grained clastites.

5.3. Probability Classes in the Proposed Categories

In theory, each category in the proposed PoS for the DBD can be assessed in the 0-1 probability range. The final decision is always made by an expert. However, standardization can be set using certain geological classes with the same probabilities that reflect the attitude of completeness for the observed variable in the virtually “infinity” number of measurements. Such categorization is previously done for hydrocarbon systems in the CPBS (Figure 1) and can be used also later for this type of PoS modification. In such case, all variables are defined with the following values: 1.00 for proven, 0.75 for highly reliable, 0.50 for fairly reliable, 0.25 for unreliable, 0.05 for an undefined variable (and 0.00 for non-existent variable, thus making PoS meaningless). Such classification purely reflects the statistical quartiles already mentioned and has been proven as successful in the previous application of the PoS in Croatia (e.g., [4,5]). Further research and analysis of particular structure case studies for HLW could lead to a larger number of events and event categories and more event probabilities. However, this could be done only when additional data are collected from the exploratory deep boreholes made intentionally for this purpose and numerous laboratory, seismic and log analysis done on the collected samples. With enough large datasets, the presented PoS can be easily benchmarked and, if necessary, improved and extended.

6. Conclusions

This study presents a modified PoS, intending to assess the safety of geological environment in deep wells, where depleted radioactive fuel could be disposed in the pre-Neogene basement of the CPBS. This is a subject of enormous importance, encompassing the regional study of the magmatic and metamorphic rocks in that area of Croatia at the regional level.

This is the first review of the northern Croatian deep subsurface for the purpose presented in this text. Therefore, an extensive introduction clarifying the subsurface geological system is considered to be extremely important for this study. Moreover, this is a conceptual study, and it was intentionally conceived in such a form. As up to date there is no real location explored for the described nuclear waste disposal purpose, real calculations cannot be performed, but the methodology behind how

such calculations can be done for the very first projects in the CPBS, can be presented. The proposed probability method can be upgraded as new results come up and benchmarking plays an important role. This means that, in this case, the PoS table can be developed and upgraded as increasingly deep wells for safe nuclear waste disposal are drilled.

Two main assumptions are initially established, the need for promising structures for waste disposal and promising lithostratigraphic units with low petrophysical values. Considering the proposed modification of PoS with the above assumptions, the classical PoS table is reassessed. Categories not fitting the scope of radioactive waste disposal are removed and new ones are created. Proposed categories and parameters for the modified PoS to be applied for radioactive waste disposal in the northern Croatia are (a) temperature, (b) sealing properties of rocks, (c) low petrophysical values + fault zone(s) inactivity and (d) subsurface fluids and aquifers. Probabilities for each category risk can range between 0.0 and 1.0. A value of 1.0 is added if all subcategory criteria are completely satisfied at the most favorable level. A value of 0.05 is added if none of the criteria is matched in the structure due to lack of data. The 0.0 value is added if data confirmed that variable is a non-existent one. The selection of probability is proposed for the descriptive categories, selected by experts, as follows: 1.00 for proven, 0.75 for highly reliable, 0.50 for fairly reliable, 0.25 for unreliable and 0.05 for an undefined variable.

This modified PoS is a regional one. No case study with the purpose of the DBD for HLW is yet performed. Hence, the first step will consist in the selection of several deep structures in the pre-Neogene basement in the Drava and Sava Depressions, based on paleostructural maps. Each of them needs to be assessed with the proposed methodology and then ranked. Such assessment will also be a benchmark of the methodology itself, making it possible to improve categories as well as the selection of critical variables.

Further development of the DBD program in Croatia depends on several research activities, mostly connected with deep drilling and laboratory measurements. It is necessary to create a database of the basement rock geomechanical properties, regionally and expressly for the most promising mapped structures. Regional stress, present-day and in the past, must be known, as well as values for geothermal heat flux and gradient variations. The sealing-borehole techniques must be tested at the samples from the northern Croatia basement. The historical earthquake activity maps would also be made, as well as palinspastic reconstruction of the major fault zones in depressions.

Author Contributions: Conceptualization, T.M., M.B., J.V., M.A.P.D., J.S. and Ž.V.; formal analysis, M.B., J.I. Investigation, U.B., M.A.P.D., M.B.; software, J.I. and M.B.; supervision, T.M., J.V. and J.S.; Validation, T.M.; visualization, M.B. and J.I.; writing—original draft, T.M., M.B., J.I., J.S., U.B., M.A.P.D., H.F.P.e.S.; writing—review and editing, T.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors are grateful for partial support from the project “Mathematical methods in geology IV” (led by T.M.). Funds were given from the University of Zagreb, for the year 2019. Authors are grateful to the Croatian Science Foundation, Project 107-F19-00013 (leader: Marijan Kovačić) for their support.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Malvić, T. Oil-Geological Relations and Probability of Discovering New Hydrocarbon Reserves in the Bjelovar Sag. Ph.D. Thesis, University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Zagreb, Croatia, 2003. (In Croatian, with Abstract in English).
2. Malvić, T. Stochastic approach in deterministic calculation of geological risk-theory and example. *Nafta* **2009**, *60*, 658–662.
3. Malvić, T.; Rusan, I. Investment risk assessment of potential hydrocarbon discoveries in a mature basin. Case study from the Bjelovar Sub-Basin, Croatia. *Oil GasEur. Mag. (Hambg.)* **2009**, *35*, 67–72.
4. Malvić, T.; Velić, J. Stochastically improved methodology for probability of success (POS) calculation in hydrocarbon systems. *RMZ-Mater. Geoenviron.* **2015**, *62*, 149–155.

5. Novak Mavar, K. Surface Transportation Modelling and Geological Aspects of Carbon-Dioxide Storage into Northern Croatian Neogene Sandstone Reservoirs, Case Study Ivanić Field. Ph.D. Thesis, University of Zagreb, Zagreb, Croatia, 2015. (In Croatian, with Abstract in English).
6. Malvić, T.; Velić, J.; Režić, M. Geological probability calculation of new gas discoveries in wider area of Ivana and Ika Gas Fields, Northern Adriatic, Croatia. *RMZ–Mater. Geoenviron.* **2016**, *63*, 127–138. [CrossRef]
7. Režić, M.; Varenina, A. A new freeware program for the Probability of Success calculation of new gas discoveries within the Croatian part of the Po depression. *Rud. Geol. Naft. Zb.* **2017**, *32*, 49–55. [CrossRef]
8. Ivšinović, J. Selection and Geomathematical Calculation of Variables for Sets with Less than 50 Data Regarding the Creation of an Improved Subsurface Model, Case Study from the Western Part of the Sava Depression. Ph.D. Thesis, University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Zagreb, Croatia, 2019. (In Croatian, with Abstract in English).
9. Malvić, T.; Ivšinović, J.; Velić, J.; Sremac, J.; Barudžija, U. Increasing Efficiency of Field Water Re-Injection during Water-Flooding in Mature Hydrocarbon Reservoirs: A Case Study from the Sava Depression, Northern Croatia. *Sustainability* **2020**, *12*, 786. [CrossRef]
10. GOVERNMENT OF THE REPUBLIC OF CROATIA. National Program for the Implementation of the Radioactive Waste, Disused Sources and Spent Nuclear Fuel Disposal Strategy (Program for the Period until 2025 with a View to 2060). *Official Gazette* **2018**, *100*, 69. Available online: https://narodne-novine.nn.hr/clanci/sluzbeni/2018_11_100_1954.html (accessed on 28 June 2020). (In Croatian).
11. ARAO & Fond NEK Third Revision of the Krško NPP Radioactive Waste and Spent Fuel Disposal Program, ver. 1.3, ARAO Doc.No. 19-1/08-01-002, FOND NEK Doc.No. 3-1/19-2-4/18. 2019. Available online: https://mzoe.gov.hr/UserDocsImages/UPRAVA%20ZA%20ENERGETIKU/Strategije,%20planovi%20i%20programi/Treca_revizija%20Programa_odlaganja_radio%20aktivnog%20goriva_i_istrosenog%20nuklearnog%20goriva%20NEK-EN.pdf (accessed on 28 June 2020).
12. CROATIAN PARLIAMENT. Radioactive Waste, Disused Sources and Spent Nuclear Fuel Disposal Strategy (Program for the Period until 2025 with a View to 2060). *Official Gazette* **2014**, 125.
13. ARAO. Inventory of SF and HLW for possible Deep Borehole Disposal-Slovenia. In *Prepared by ARAO for the Purpose of ERDO Joint Project on Deep Borehole Disposal Lead by NND Norway*. 20-08-004-001; Croatian Geological Survey: Ljubljana, Slovenia, 2011; p. 19.
14. Galamboš, M.; Rosskopfová, O.; Kučáková, J.; Rajec, P. Utilization of Slovak bentonites in deposition of high-level radioactive waste and spent nuclear fuel. *J. Radioanal. Nucl. Chem.* **2011**, *288*, 765–777. [CrossRef]
15. Adamcová, R.; Suraba, V.; Krajňák, A.; Rosskopfová, O.; Galamboš, M. First shrinkage parameters of Slovak bentonites considered for engineered barriers in the deep geological repository of high-level radioactive waste and spent nuclear fuel. *J. Radioanal. Nucl. Chem.* **2014**, *302*, 737–743. [CrossRef]
16. *Geological Map of the Republic of Croatia at a Scale 1:300.000*; Croatian Geological Survey: Zagreb, Croatia, 2009; Available online: <http://webgis.hgi-cgs.hr/gk300/default.aspx> (accessed on 28 June 2020). (In Croatian)
17. *Guide to the Geological Map of the Republic of Croatia at a scale 1:300.000*; Velić, I.; Vlahović, I. (Eds.) Croatian Geological Survey: Zagreb, Croatia, 2009; p. 141. (In Croatian)
18. Šikić, K. Prikaz geološke građe Medvednice [Overview of geological structure of the Medvednica Mt.]. In *Geološki Vodič Medvednice [Geological Guide for Medvednica Mt.]*; Šikić, K., Ed.; Croatian Geol. Institute & INA Petroleum Comp.: Zagreb, Croatia, 1995; pp. 7–40. (In Croatian)
19. Fuček, L.; Tišljarić, J.; Sokač, B.; Prtoljan, B.; Oštrić, N. Upper Triassic dolomites in Podsused Quarry (Stop 1). In *Geological Guide for Medvednica Mt*; Šikić, M., Ed.; Croatian Geological Institute & INA Petroleum Comp.: Zagreb, Croatia, 1995; pp. 41–43. (In Croatian)
20. Tomljenović, B. Structural Characteristics of Medvednica and Samoborsko Gorje Mountains. Ph.D. Thesis, University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Zagreb, Croatia, 2002. (In Croatian, with Abstract in English).
21. Maričić, A.; Starčević, K.; Barudžija, U. Physical and mechanical properties of dolomites related to sedimentary and diagenetic features—case study of the Upper Triassic dolomites from Medvednica and Samobor Mts., NW Croatia. *Rudarsko-geološko-naftni Zb. (Mining-Geological-Petroleum Eng. Bull.)* **2018**, *33*, 33–44. [CrossRef]
22. Grgasović, T. Stratigraphy of the Upper Triassic deposits of Žumberak. Master of Science Thesis, University of Zagreb- Faculty of Science, Zagreb, Croatia, 1998. (In Croatian, with Abstract in English).

23. Pavičić, I.; Dragičević, I.; Vlahović, T.; Grgasović, T. Fractal analysis of fracture systems in Upper Triassic Dolomites in Žumberak Mountain, Croatia. *Rudarsko-geološko-naftni Zb. (Mining-Geological-Petroleum Eng. Bull.)* **2017**, *32*, 1–13. [\[CrossRef\]](#)
24. Barudžija, U.; Velić, J.; Malvić, T.; Trenc, N.; Matovinović Božinović, N. Morphometric Characteristics, Shapes and Provenance of Holocene Pebbles from the Sava River Gravels (Zagreb, Croatia). *Geosciences* **2020**, *10*, 92. [\[CrossRef\]](#)
25. Barudžija, U.; Bočić, N.; Macek, K.; Repinc, I.; Smirčić, D. Triassic carbonate complex of the Papuk Mts. (Outcrops along Velika—Slatinski Drenovac road). In *5th Croatian Geological Congress—Fieldtrip Guidebook*; Horvat, M., Galović, L., Eds.; Croatian Geological Survey: Zagreb, Croatia, 2015; pp. 55–64.
26. Šegvić, B. Petrology and Geochemistry of the Greenschists from the Central Part of the Medvednica Mts. Master of Science Thesis, University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Zagreb, Croatia, 2003. (In Croatian, with Abstract in English).
27. Mišur, I. Geodinamic Evolution of Low-Grade Metamorphism Metasedimentary Rocks in the Medvednica Mts. Ph.D. Thesis, University of Zagreb, Faculty of Science, Zagreb, Croatia, 2017. (In Croatian, with Abstract in English).
28. Šuica, S. Granitoids of the Pannonian Basin Basement in the Eastern Croatia. Ph.D. Thesis, University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Zagreb, Croatia, 2019. (In Croatian, with Abstract in English).
29. Malvić, T. Strukturni i Tektonski Odnosi te Značajke Ugljikovodika Širega Područja Naftnoga Polja Galovac-Pavljani [*Structural and tectonic relations and characteristics of hydrocarbons in the wider area of the Galovac-Pavljani oil field*]. Master of Science Thesis, University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Zagreb, Croatia, 1998. (In Croatian, with Abstract in English).
30. Malvić, T. Regional geological settings and hydrocarbon potential of Bjelovar sag (subdepression), R. Croatia. *Nafta* **2004**, *55*, 273–288.
31. Malvić, T. Review of Miocene shallow marine and lacustrine depositional environments in Northern Croatia. *Geol. Q.* **2012**, *56*, 493–504. [\[CrossRef\]](#)
32. Pavelic, D. Tectonostratigraphic model for the North Croatian and North Bosnian sector of the Miocene Pannonian Basin System. *Basin Res.* **2001**, *13*, 359–376. [\[CrossRef\]](#)
33. Pavelic, D.; Miknic, M.; Sarkotic Šlat, M. Early to Middle Miocene facies succession in lacustrine and marine environments on the southwestern margin of the Pannonian basin system. *Geol. Carpathica* **1998**, *49*, 433–443.
34. Vrbanc, B. Paleostrukturne i Sedimentološke Analize Gornjopanonskih Naslaga Formacije Ivanić Grad u Savskoj Depresiji [*Paleostructural and sedimentological analyzes of the Upper Pannonian deposits of the Ivanić grad Formation in the Sava Depression*]. Ph.D. Thesis, University of Zagreb, The Faculty of Science, Zagreb, Croatia, 1996. (In Croatian, with Abstract in English).
35. Prelogovic, E. Neotektonska karta SR Hrvatske [*Neotectonic map of SR Croatia*]. *Geol. Vjesn.* **1975**, *28*, 97–108. (In Croatian)
36. Malvić, T.; Cvetković, M. Lithostratigraphic units in the Drava Depression (Croatian and Hungarian parts)—A correlation. *Nafta* **2013**, *64*, 27–33.
37. Malvić, T. Geological maps of Neogene sediments in the Bjelovar Subdepression (northern Croatia). *J. Maps* **2011**, 304–317. [\[CrossRef\]](#)
38. Pandžić, J. Podloga tercijara jugozapadnog dijela Panonskog bazena [*Tertiary base of the southwestern part of the Pannonian Basin*]. In Proceedings of the IV. God. Znanstvenog Skupa I. Sekc. ZSN JAZU—Stubičke Toplice, Zagreb, Croatia, 1978; pp. 33–44. (In Croatian).
39. Hernitz, Z. Dubinski Strukturno-Tektonski Odnosi u Području Istočne SLAVONIJE [*Deep structural-tectonic relations in the area of Eastern Slavonia*]. Ph.D. Thesis, University of Zagreb, Zagreb, Croatia, 1983. (In Croatian).
40. Malvić, T. Geološki Odnosi Područja Virovitica-Rezovačke Krčevine-Orešac [*Geological relations of the area Virovitica-Rezovačke Krčevine-Orešac*]. Master's Thesis, University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Zagreb, Croatia, 1995. (In Croatian, with Abstract in English).
41. Malvić, T.; Sučić, A.; Cvetković, M.; Resanović, F.; Velić, J. Low permeability Neogene lithofacies in Northern Croatia as potential unconventional hydrocarbon reservoirs. *Cent. Eur. J. Geosci.* **2014**, *6*, 182–194. [\[CrossRef\]](#)
42. Cota, L.; Britvić, V. Hidrodinamika i kemizam formacijskih voda Dravske potoline—Panonski bazen [*Hydrodynamic and chemistry of Drava Depression formation waters—Pannonian Basin*]. *Nafta* **1991**, *42*, 121–136. (In Croatian, with Abstract in English).

43. Malvić, T. Ležišne vode naftnoga polja Galovac-Pavljani [*Field water of the Galovac-Pavljani Field*]. *Hrvat. Vode* **1999**, *7*, 139–148. (In Croatian)
44. Malvić, T.; Velić, J. Relation between Effective Thickness, Gas Production and Porosity in Heterogeneous Reservoirs: An Example from the Molve Field, Croatian Pannonian Basin. *Pet. Geosci.* **2010**, *16*, 41–51. [[CrossRef](#)]
45. White, D.A. Geologic Risking Guide for Prospects and Plays. *AAPG Bull.* **1993**, *77/12*, 2048–2061. [[CrossRef](#)]
46. Hernitz, Z.; Bokor, N.; Malvić, T. Probability Evaluation of New Hydrocarbon Finds in Some Parts of Sava and Drava Depression. In Proceedings of the Working materials of the 2nd Int. Symposium on Petroleum Geology, Zagreb, Croatia, 22–24 April 1999; pp. 165–175.
47. Malvić, T.; Rusan, I. Potential hydrocarbon discoveries in Bjelovar Subdepression, Croatia. *Search Discov.* **2007**, *9*, 1–6.
48. Beswick, A.J.; Gibb, F.G.F.; Travis, K.P. Deep borehole disposal of nuclear waste: Engineering challenges. *Energy* **2014**, *167*, 47–66. [[CrossRef](#)]
49. Wang, J. On area-specific underground research laboratory for geological disposal of high-level radioactive waste in China. *J. Rock Mech. Geotech. Eng.* **2014**, *6*, 99–104. [[CrossRef](#)]
50. Zhao, X.G.; Wang, J.; Qin, X.; Cai, M.; Su, R.; He, J.; Zong, Z.; Ma, L.; Ji, R.; Zhang, M.; et al. In-situ Stress Measurements and Regional Stress Field Assessment in the Xinjiang Candidate Area for China's HLW Disposal. *Eng. Geol.* **2015**, *197*, 42–56. [[CrossRef](#)]
51. Gibb, F.G.F.; Travis, K.P.; McTaggart, N.A.; Burley, D.; Hesketh, K.W. High density support matrices: Key to deep borehole disposal of spent nuclear fuel. *J. Nucl. Mater.* **2008**, *374*, 370–377. [[CrossRef](#)]
52. Macenić, M.; Kurevija, T.; Strpić, K. Systematic review of research and utilization of shallow geothermal energy in Croatia. *Rudarsko-geološko-naftni Zb. (Mining-Geological-Petroleum Eng. Bull.)* **2018**, *33*, 37–46. [[CrossRef](#)]
53. Borović, S.; Marković, T.; Larva, O.; Brkić, Ž.; Mraz, V. Mineral and Thermal Waters in the Croatian Part of the Pannonian Basin. In *Mineral and Thermal Waters of Southeastern Europe*; Papić, P., Ed.; Springer: Berlin/Heidelberg, Germany, 2016; pp. 31–45, 174.
54. Franklin, W.S.; Yongje, K.; Byung-Gon, C. Deep Borehole Disposal of Nuclear Wastes: Opportunities and Challenges. *J. Nucl. Fuel Cycle Waste Technol.* **2017**, *15*, 301–312. [[CrossRef](#)]
55. U.S. Nuclear Waste Technical Review Board (NWTRB). Technical evaluation of the U.S. Department of Energy deep borehole disposal research and development program. In *A Report to the U.S. Congress and the Secretary of Energy*; NWTRB: Arlington, VA, USA, 2016.
56. Tatarinov, V.N.; Morozov, V.N.; Manevich, A.I.; Tatarinova, T.A. Underground Research Laboratory: To the Program of Geomechanical Research. *Radioact. Waste* **2019**, *2*, 82–96. [[CrossRef](#)]
57. Gibb, F.G.F.; Travis, K.P.; McTaggart, N.A.; Burley, D. A model for heat flow in deep borehole disposals of high-level nuclear waste. *J. Geophys. Res.* **2008**, *113*, B05201. [[CrossRef](#)]
58. Gibb, F.G.F.; Travis, K.P.; Hesketh, K.W. Deep borehole disposal of higher burn up spent nuclear fuels. *Mineral. Mag.* **2012**, *76*, 3003–3017. [[CrossRef](#)]
59. Brady, P.V.; Arnold, B.W.; Freeze, G.A.; Swift, P.N.; Bauer, S.J.; Kanney, J.L.; Rechard, R.P.; Stein, J.S. *Deep Borehole Disposal of High-Level Radioactive Waste*; SAND2009-4401; Sandia National Laboratories: Albuquerque, NM, USA, 2009; p. 74.

