

Article

Development of a Low-pH Concrete Intended for Deep Geological Repository for Radioactive Waste

Radka Pernicova ^{1,*}, David Citek ¹, Daniel Dobias ¹, Jiri Kolisko ¹, Tomas Mandlik ¹ and Lucie Hausmannova ²¹ Klokner Institute, Czech Technical University, Solinova 7, 166 08 Prague, Czech Republic² Radioactive Waste Repository Authority—SÚRAO, Dlazdena 6, 110 00 Prague, Czech Republic

* Correspondence: radka.pernicova@cvut.cz

Abstract: This article deals with the development of concretes intended to be used as construction materials in the Czech deep repository for radioactive waste. The basic requirements for this concrete are a reduced pH value, which must maintain a constant reduced pH with a value of around 11 in the long term, and mechanical properties comparable to conventional concrete. The raw materials for the production of the proposed low pH concrete come exclusively from the Czech Republic. Material characteristics were measured on fresh mixtures and concrete after 28, 56, and 90 days of curing. In addition to the basic raw materials (aggregate, cement, water), plasticizers, microsilica or slag, and defoaming agents were added to the mixture. The aggregate:binder ratio was approximately 5:1 and the w/c water coefficient was approximately 0.6. The mechanical properties of the final concrete were similar to the reference recipe of conventional concrete (the decrease was less than 10%) and the pH value was even below 11 after 90 days. The issue of a sprayed variant of the LPC mixture was solved within the project.

Keywords: pH; concrete; durability; strength; deep geological repository



Citation: Pernicova, R.; Citek, D.; Dobias, D.; Kolisko, J.; Mandlik, T.; Hausmannova, L. Development of a Low-pH Concrete Intended for Deep Geological Repository for Radioactive Waste. *Buildings* **2023**, *13*, 182. <https://doi.org/10.3390/buildings13010182>

Academic Editor: Ahmed Senouci

Received: 14 December 2022

Revised: 5 January 2023

Accepted: 7 January 2023

Published: 10 January 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The issue of storing high-level activity waste and spent nuclear waste is a hot topic in many countries; the first storage of this waste should be operational in 2025 in Finland [1]. At present, depositing waste in stable rocks is considered to be the most suitable variant, where the waste will be secured (isolated from the biosphere) for a long time both by the rock itself and by a system of engineering barriers [2]. As it is a radioactive material with a long half-life, it is necessary to ensure the safety of its storage for hundreds of thousands of years.

All countries that use nuclear power are forced to consider how to solve the question of the disposal of radioactive waste and spent nuclear fuel. Scientists around the world agree that building a deep geological repository (DGR in short) is the safest solution to protect the environment for hundreds of thousands of years [3]. All countries that produce high-level activity waste and spent nuclear fuel must take care of these materials themselves, and the Czech Republic is also moving towards the construction of such a repository [4].

DGRs work based on a system of engineered and geological barriers. The most significant barrier consists of 500 m of stable rock, which, in combination with the engineered barriers, shields the biosphere from radioactivity over a period of hundreds of thousands of years. Although in terms of human existence this is an unimaginably long time, certain geological formations remain unchanged even over hundreds of millions of years. Several types of rocks are being studied around the world, which in specific geological conditions can be assumed to have the required properties.

The Czech concept is based on storage in crystalline rocks, where the waste will be placed in steel storage sets and sealed with bentonite, which will also be used as a filler for the remaining underground spaces, in a borehole at a depth of 500 m underground

(see Figure 1) [5]. The technical solution for the repository is still under development. The vertical system involves vertical disposal wells drilled from horizontal disposal tunnels; the diameter of 1.8 m and a depth of around 5.5 m for VVER-440 container type, respectively, and 7.2 m for VVER-1000. The horizontal disposal system contains horizontal microtunnels with a diameter of 2.2 m; their maximum length is 300 m [6].

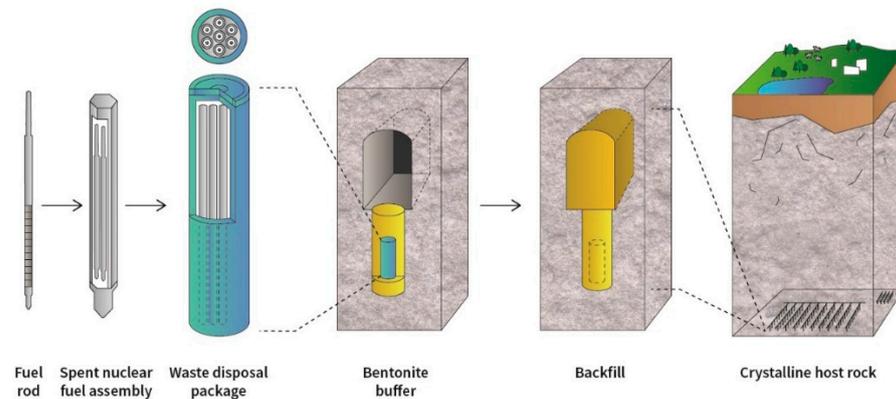


Figure 1. The concept of the Czech deep repository [5].

The other, i.e., engineered barriers consist of a double-skinned metal waste container, a special clay (bentonite) buffer and backfill material, and concrete structures. The selection of the most suitable materials for the production of the waste container will be based on the results of intensive research on the properties of various metals. The containers will be hermetically sealed and backfilled with the bentonite mixture, which is both inert and impermeable to water. Moreover, research to date indicates that bentonite is able to retard the transport of radionuclides for up to several tens of thousands of years. Moreover, the design of a container for spent nuclear fuel is under development; 12 variants have been considered [7]. The most studied variety is a double-walled steel-based canister, with an outer wall from carbon steel and inner pouches from stainless steel. Concerning the buffer and backfill concept, the basic design was proposed, but searching for alternatives is ongoing. The basic concept for the buffer involves the combination of compacted bentonite blocks and pellets. The design of the backfill is based on the bentonite material; however, a mixture of bentonite and crushed rock can also be used. Currently, the solution for the Czech Republic is that bentonite will be used as the buffer and also as a backfill material. That is the reason why has been extensively tested in recent years [8]. This bentonite (Ca–Mg type with a higher amount of iron in the octahedral positions) is mined in the western part of Czechia [9].

This system will also be supplemented by other structural elements such as plugs separating individual sections, linings, and grouting. These structural elements will perform their function only during the operation of the repository, but after its closure, it is necessary that these elements do not affect the properties of engineering barriers adversely. Concrete will be used for most structural elements, which is a tested material in underground construction. Some of these concrete elements are of a fixed shape, and therefore can be created in a laboratory/company and brought as ready-made product to the DGR site. Other constructions, for example, covering of the wall or plugs, must be solved on the spot in the form of shotcrete [10]. However, concrete is specific for its pH, whose values range from 12.5 to 13.5, and with contact of the ground waters creates a pore water leachate with a pH around 13 [11]. For the stability of bentonite, as a material of one of the engineering barriers, such a high pH is unfavorable and could degrade its properties [12].

Undesirable geochemical processes that can change material properties were observed on the concrete/bentonite interface. [13] In the vicinity of this interface, magnesium silicate hydrates M-S-H and calcium silicate hydrates C-S-H could form. These crystallization phases, which most likely can be related to the decalcification of concrete, can cause a loss of swelling ability or a change in porosity and diffusion properties [14]. The size and scope

of changes is caused by the very nature of the cement material [15]. Given the complexity of the proposed DGR, it is easier to change the properties of concrete than to look for a new buffer material instead of bentonite. Therefore, concrete that retains a long-term pH value of around 11 has to be developed [16]. This value is especially required for its characteristics to approximate properties of bentonite, so that it can perform its function in the deep repository for a long time [17]. At the same time, it also affects the resistance of concrete to granitic groundwater exposure [18].

The key issue of low pH is the binder composition of the concrete, time, and methods of pH measurement. The most important requirements for the concrete, besides low pH, are good processability of the mixture, low shrinkage, and low hydrating heat [19]. Parameters such as compressive and tensile strengths or a modulus of elasticity test are also determined on concrete [20].

All concrete recipes have a similar pH after mixing, regardless of the binder composition. However, with increasing time, the pH value decreases [18,21,22]. The steepness of the drop and the resulting value of the long-term stabilized pH depend on the selected binder and added chemical admixtures. In most samples, the pH stabilizes after about 3 months of age [16].

In order to achieve a lower pH, it is necessary to replace approximately 50% of the cement with other active ingredients such as pozzolanas, microsilica, fly ash, or slag [23–25]. To reduce the pH, it is necessary to increase the SiO₂ content of the mixture. The SiO₂-based binder has finer grains, and therefore better fills the space between larger cement grains. The resulting concrete is therefore denser, and as a result has better mechanical properties such as compressive strength.

When designing mixtures, it is important to determine the so-called Ca/Si ratio, which is the ratio of calcium and silicon content in the mixture [26]. Substituting cement by the mineral additives with high silica content decreases the calcium hydroxide formation in the binder and significantly changes the microstructure compared to ordinary concrete. The resulting C-S-H gels with low Ca/Si ratios are formed by longer-length chains of tetrahedral silica [27]. The binding process during hydration removes the alkalis from the pore solution of low-pH pastes. This process is more effective when the Ca/Si ratios of C-S-H gels are between 1.2 and 0.85 [28]. The chemically stable concrete should not have a ratio of less than 0.6. The optimum recommended value for concretes with low pH is in the range of 0.6–1.0 (preferably around 0.8) [16].

Not only the choice of binder but also the specific type of filler and its properties can affect the resulting pH of the mixture [20]. The recommended ratio of gravel to sand is around 1.1. Feldspar or basalt, which have up to 53% SiO₂, are especially mentioned as suitable aggregates for these concretes [29].

In addition to measuring pH, it is necessary to determine the basic properties of these mixtures. The most important characteristics of a fresh mixture include its processability (in most cases, self-compacting concrete is required) and low hydrating heat. In the case of hardened samples, the mechanical properties, shrinkage, absorbency, and permeability for chlorides and sulfates are determined [30].

This paper deals with the design formula of low-pH concrete with high ratio of microsilica suitable for being used in radioactive waste repositories. In addition to the ratio selection of active materials in the binder, the methodical procedure of testing is equally important. Verification of the suitable designed mixture is always a process that includes many tests and measurements, which should be examined in the long term. Due to the variety of raw materials, it is not possible to take over the previously designed LPC recipes and it is necessary to test their suitability for use in a given locations.

Therefore, thanks to the appropriate composition of an accurate sequence and the importance of individual tests, there is no need to go through the entire verification process for all those proposed recipes. Such a flow chart is a part of this article. The last part of this paper contains the practical part, where the application of the designed mixture in the form of dry spraying in a DGR was verified.

2. Materials and Methods

The primary composition of concrete formulations is based on previous research elaborated in article [31], which deals with the initial design of the formulation on cement mortars. As other active ingredients instead of cement, slag and microsilica were selected: slag for its ability to increasing the chemical stability of the mixture, and microsilica for its for its high fineness of grinding, which causes a change in porosity in the mixture and thus reduces permeability and increases mechanical strength.

A mixture proposal with a high proportion of microsilica (51% of the binder), a low proportion of slag (9% of the binder), and a Portland cement (OPC) content (40% of the binder) appeared to be the best. Plasticizers were further added to the mixture to make it more processable [32].

Formulations marked 1A and 1B were then based on this design, which were further modified to create formulations marked 2A and 2B. Mixtures 1A and 1B had to be modified because they had a very low cone sump (almost zero), and the concrete mix would be practically unprocessable. In formulation 2A, there had to be an increase in very fine and fine aggregate (fraction 0/4 and fraction 4/8) and a reduction in coarse aggregate (fraction 8/16), and the volume of batch water was increased in response to this change. In order to maintain the filler:binder ratio, formulation 2B was proposed, where the amount of binder was increased, and the amount of aggregate was reduced. Subsequently, the amount of water was increased to maintain a water–cement ratio w/c .

As the consistency and processability of the fresh mixture was improved for the concrete 2A and 2B, an undesirable problem with the air content in the mixture occurred. The air content was too high, and the strength characteristics of the concrete could be reduced due to the higher porosity. This side effect was eliminated by further modification in the area of aggregate and water and by the use of a defoamer (see formulation 3, which was assumed to meet the basic characteristics of ordinary concrete, and which was selected as the final recipe). Mixture 3 was produced in large-volume casting on the TBG Metrostav s.r.o. company premises. The proposed composition of the mixtures is given in Table 1. The dosage of the fresh mixture is always given in kg per 1 m³ of mixture. All raw materials come from the Czech Republic.

Table 1. Composition of the mixtures.

Material (kg)	REF	1A	1B	2A	2B	3
Sand 0–4	885	880	840	935	868	895
Aggregate 4/8	360	375	340	432	401	413
Aggregate 8/16	605	605	570	422	392	404
CEM I 42.5 R Cement	300	120	160	120	140	140
Microsilica	-	153	204	153	179	179
Slag	-	27	36	27	32	32
Water	130	130	170	170	180	200
Plasticizer	6	6	6	6	7	7
Defoamer	-	-	-	-	-	1.75

Cement is the most common hydraulic binder and one of the main raw materials for the production of concrete or mortar. Portland cement is produced by burning limestone with clay and possible secondary raw materials with additions of gypsum after burning [33,34]. CEM I 42.5 R cement produced in the Mokra cement plant in the Czech Republic was evaluated as the most suitable. Microsilica is formed as a by-product in the production of ferroalloys or elemental silicon. The particles are about a hundred times smaller than the cement grains, and due to their fineness, the space between the coarser cement grains is better filled. Thanks to the presence of microsilica, the concrete is stronger [35]. Ground granulated blast furnace slag (GGBFS) is formed as a by-product in the production of iron. Due to the presence of slag, concretes are resistant to, for example, seawater or

environments with a high incidence of sulfates and other aggressive agents. The addition of slag to concrete increases its durability, strength and heat resistance. Slag contains 30–50% of CaO, 30–45% of SiO₂, 5–20% of Al₂O₃, and 1–15% of MgO, and it further contains iron oxides, sulfides, or manganese oxide [36]. The slag comes from the Dětmarovice production plant of CEMEX Czech Republic s.r.o. in the Czech Republic. Plasticizers are admixtures that increase the flowability or plasticity of materials. Plasticizers that are added to concrete improve the processability of fresh concrete or reduce the amount of water needed to achieve better processability. In general, the plasticizer proportion is between 1 and 2 wt.% of the binder. The use of a plasticizer and a smaller amount of water leads to higher strengths of concrete with the same processability of the fresh mixture [37]. Used plasticizer was polycarboxylate ether material-based (commercial name MASTERGLENIUM ACE 300). Defoaming agents displace air from the concrete, which increases the density of concrete. An increase in density is associated with an increase in resistance of the concrete surface, or resistance to the formation of lime efflorescence. If a defoamer is added to the concrete, the concrete has a smooth surface without pores and bubbles [37]. It was blend of defoamer components on silica base (commercial name AGITAN[®] P 841). Due to the complexity of the radioactive waste storage system, it is necessary to limit the content of organic components in the proposed mixture. If they are above the limit, the complexity could be disrupted, and the system could appear ineffective after some time. The sum of all organic substances in the dry powder state (defoamer + plasticizer) ranged from 1.5 to 2 wt.% of the total amount of binder, which is the usual value reported in the currently available output of similar research [33].

All samples were kept in the mold for a minimum time (24 h) after casting. The method of further treatment after demolding depended on the test for which the given samples were intended. To measure the mechanical properties, absorbency, and maximum penetration depth, the samples were kept in water storage (drinking water at 20 ± 2 °C) until one day before the test itself. Samples for shrinkage were removed from the mold after 24 h and left in air, maintaining the relative humidity at about 50% and the temperature between 20–25 °C. The sample for measuring the hydrating heat had the dimensions of a cube with an edge of 300 mm and was cast into special molds, which were isolated from the external environment and contain temperature sensors. They remained in these molds throughout the whole measurement period, i.e., until 28 days after mixing.

The first five mixtures were manufactured and tested under laboratory conditions at a temperature of 20 ± 2 °C. The final mixture, marked as 3, was produced in a large capacity directly in the concrete plant in order to test the uniformity of the concrete.

2.1. Methods for Testing the Measured Quantities

Concrete characteristics were identified on fresh mixtures and concrete. The volumetric mass density of fresh mixtures and concrete was measured. The fresh mixtures were further tested for cone sump, air content, or concrete temperature during mixing, and concrete was tested for strength characteristics, absorbency, or shrinkage. During the setting and hardening process, the development of temperatures during the hydration of the cement was measured.

2.1.1. Fresh Mixture

From the basic physical properties, the volumetric mass density of the mixture was measured according to EN 12350-6 [38]. The principle of the fresh concrete volumetric mass density test was the compacting of fresh concrete in a rigid and waterproof vessel of known volume and weight and subsequent weighing. To determine the weight m_1 of the vessel, it was weighed, and the value was recorded. Depending on the consistency of the concrete and the compaction method, the vessel was filled in two or more layers to achieve complete compaction. The volumetric mass density of fresh concrete was rounded to the nearest 10 kg/m³.

Air content test was performed in accordance with EN 12350-7 [39]. The test vessel was filled with concrete in three layers of approximately the same thickness. Immediately after placing the layer into the vessel, the concrete was compacted to achieve complete compaction. The vessel and lid flange were cleaned thoroughly. The lid was attached to the vessel with clamps and then the valves for inflow and discharge of water were opened. The instrument was filled with water until water flows out of the second valve. The instrument was tapped with a mallet to remove air bubbles. The valves for discharge and drainage of water from the air chamber were closed and air was pumped into the air chamber until the pressure gauge needle shows the initial pressure value. Alternatively, this could be achieved with the reduction button. The main air valve was then opened with the start button. The pressure value corresponding to the percentage of air contained was read on the pressure gauge.

2.1.2. Concrete

From the basic physical properties of the samples, the volumetric mass density was measured after 28 days of curing. The volumetric mass density was determined according to EN 12390-7 [40]. The volumetric mass density was measured on samples determined for strength characteristics, i.e., just before the compressive strength test was performed on the concrete.

Concretes were measured in terms of a decrease in pH after 28, 56 and 90 days after preparation of the mixture. A leaching method using distilled water as the medium was chosen for pH test [41]. After a given time, the specimen was dried and ground to analytical fineness. Subsequently, an aqueous leach was made from the sample in distilled water. The resulting solution was mixed in a 1:1 weight ratio (50 g of sample with 50 mL of distilled water). Leaching was performed for 5 min under laboratory conditions ($t = 22 \pm 3 \text{ }^\circ\text{C}$, $\text{RH} = 40\%$). After this time, suspension of the given sample was analyzed by a pH meter with glass electrode (inoLAB Multi 9420 pH multimeter).

The cubic compressive strength test was performed according to EN 12390-3 [42]. After 24 h, the samples with a size of 150 mm were removed from the molds and stored in drinking water at a temperature of $20 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$. One day before the test itself, the specimens were stored in air at $23 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$. Compressive strength f_c [MPa] was determined on these standard cubes after 28 days of curing.

The four-point bend tensile strength test was performed according to EN 12390-5 on samples with dimension of $100 \times 100 \times 400$ mm [43]. After one day, the samples were removed from the molds and stored in an aquatic environment. One day before the test itself, the specimens were stored in laboratory at temperature $23 \pm 2 \text{ }^\circ\text{C}$. The samples were placed perpendicular to the compaction direction on supports with a spacing of 300 mm. The load was transmitted through the load cylinders at a constant speed. The result was the maximum value of the force achieved when the sample broke.

The principle of the test for the determination of the static modulus of compressive elasticity according to ISO 1920-10 [44] was to expose the sample to a tension of 0.5 MPa and of one-third of the compressive strength of concrete. The relative strains at the corresponding tensions were then recorded. The modulus of elasticity was calculated by dividing the difference between the basic tension and the upper load tension by the difference in the corresponding strains.

The test piece with axially mounted instruments was placed centrally in the testing machine. A basic tension σ_b of 0.5 MPa was applied and maintained for 60 s, and then the readings on all instruments were read and recorded. The tension was continuously increased until it equaled 1/3 of the cylindrical compressive strength. The tension was kept on this value for 60 s. If the individual measurements were not within a range of $\pm 20\%$ of their mean value, the test was repeated.

The absorbency test was performed according to the ČSN 73 1316 standard [45]. The test samples were placed in a tap water vessel so that their height was as low as possible. The vessel must be at least 5 cm taller than the inserted samples. Water was poured into the

vessel so that the test samples were dipped to a height of 3 cm. Water was added evenly every hour so that after three hours the water level was around 1 cm above the sample surface. The water level was maintained at a level of around 1 cm above the sample surface throughout the sample soaking period. The test samples were saturated to a state in which they no longer absorbed water. The test samples were carefully wiped before weighing so that the concrete surface was evenly damp. The saturation of the samples was complete if no measurable weight was gained in the last 24 h. After completion of saturation and weighing, the test samples were dried to a stable weight at a temperature of 105–110 °C.

Furthermore, the hydrating heat released was determined. The object of the test was to determine the highest temperature reached due to cement hydration. The measurement was performed on all concrete formulations. Measurements were performed using Pt1000 resistance temperature sensors. The temperature sensors were connected to a Comet S0141 datalogger. The temperature reading was performed continuously every 5 min. The expanded temperature measurement uncertainty was ± 0.5 °C. A 300 mm cube was used for the tests, cast into a mold made from 20 mm thick waterproof plywood, which was insulated from the surrounding environment by polystyrene of 100 mm thickness on all sides. The outer wall of the mold was again made of 20 mm thick waterproof plywood. A sensor to record the temperature of the concrete was placed into the center of the sample, and another sensor recorded the temperature of the environment.

3. Results

After mixing, the tests were first performed in the laboratory on fresh concrete, then the concrete was poured into molds and allowed to harden for 28 days. The properties of the resulting concrete produced according to formulation 3 were measured in a large-volume concrete plant. The consistency of the mix was optimized to achieve better properties of both fresh mixture and concrete.

3.1. Fresh Mixture Properties

The following properties were measured on fresh mixtures: volumetric mass density, fresh air content, cone sump, and concrete temperature during mixing. The results are summarized in the Table 2.

Table 2. Fresh concrete mixture properties.

Mixtures	Volumetric Mass Density (kg/m ³)	Fresh Air Content (%)	Cone Sump (mm)	Mixing Temperature (°C)
REF	2340	4.2	7.5	20.8
1A	2240	5.1	0	20.6
1B	2270	2.2	0	21.8
2A	2060	11.4	130	20.0
2B	2110	8.0	130	19.7
3	2280	2.4	130	19.2

First, the reference mixture (labeled REF) was mixed, which was based on the initial design in the article [31]. However, this mixture did not contain other additives such as microsilica, slag, etc. Then mixtures 1A and 1B were mixed and tested. Mixtures marked with the number 1 showed very low values of cone sump and the mixtures were not well processable. When modifying the mixtures, a uniform water coefficient w/c was chosen. In formulation 2A, the content of binder (cement, microsilica, and slag) was increased compared to 1A and the content of aggregate and sand was reduced. In formulation 2B, the binder content was reduced, and the aggregate content was increased compared to 1B.

The cone slump values were directed towards consistency class S3 (100–150 mm). The higher the number, the more fluid the consistency of the mixture. The values of the cone sump of concretes 2A and 2B were 130 cm, which was already in the required category.

However, these mixtures had a high air content (the limit value is up to 5%, and in mixture 2A there was 8.0% air and in mixture 2B there was 11.4% air). If the air content in the mixtures is too high, its strength characteristics deteriorate. Therefore, a defoamer was added to mixture 3. The content of fresh air in this mixture was then the norm, namely 2.4%. The appropriate and accurate time sequence of individual tests is really important to not need to go through the entire verification process for all mixtures. Therefore, it was design flow chart of Materials and Methods for design of concretes recipes (see Figure 2).

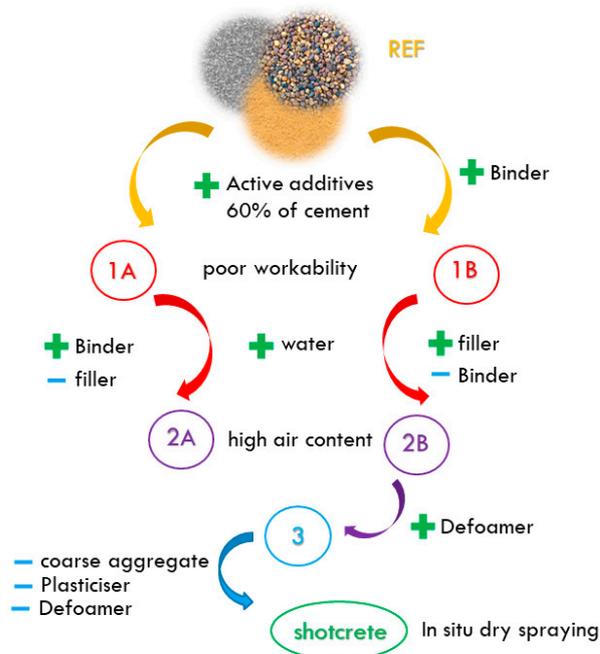


Figure 2. Flow chart of Materials and Methods for design of mixtures.

The properties of the fresh concrete mixture in the resultant formulation 3 from large-volume casting already matched the characteristics of commercially available concrete with normal pH values. The temperature of the fresh concrete during mixing was approximately the same in all tested mixtures, around 20 °C. Volumetric mass density ranged from 2000 to 2300 kg/m³.

3.2. Concrete Properties

The following tables and graphs summarize the results of individual measurements on concrete after 28, 60, and 90 days from mixing.

The following Figure 3 shows the volumetric mass density of the concrete. Samples 2A and 2B, which contained more binder and less aggregate, showed a lower volumetric mass density than the samples numbered 1. The density of the sample increased again with the addition of the defoamer. In all cases, the volumetric mass density was constant after 28 days and changed with a deviation of 0.9% (see Figure 3).

The basic concrete characteristic tested was the pH value measured depending on the time from mixing. The results are shown in the graph in Figure 4. All designed concretes, including the large-volume casting sample, had a pH of about 11 measured 90 days after curing. The red line in Figure 3 indicates the maximum limit value of 11.2, below which the resulting pH values should be in the long term.

The results for concrete compressive strengths are summarized in Figure 5. Samples 1A and 1B showed similar compressive strengths as the concrete reference sample. Samples with a higher water and pore content (marked 2A and 2B in the Figure) show a significant reduction in strength.

The tensile strength of sample 1B improved by about 25% and that of sample 1A increased by 11% compared to the reference sample. The modified formulations (2A, 2B)

had the tensile strength 22% and 26% lower than the reference sample, respectively (see Figure 6).

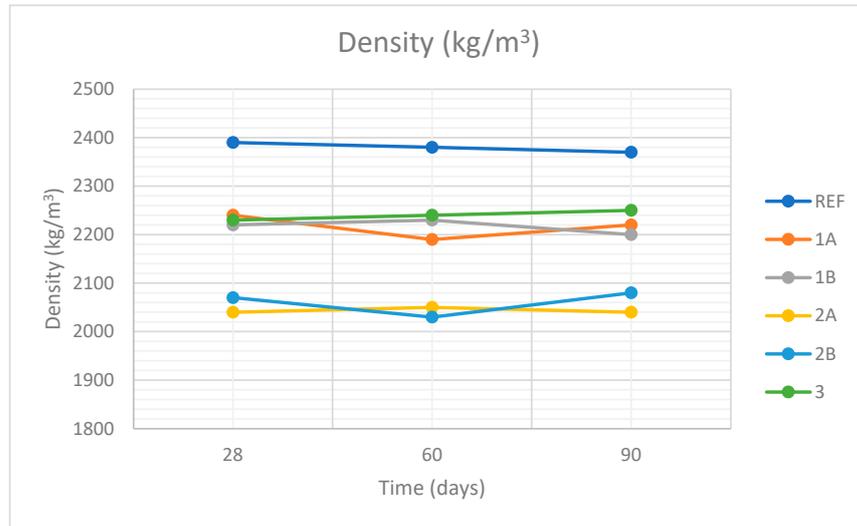


Figure 3. Volumetric mass density of concrete, measured after 28, 60, and 90 days from mixing.

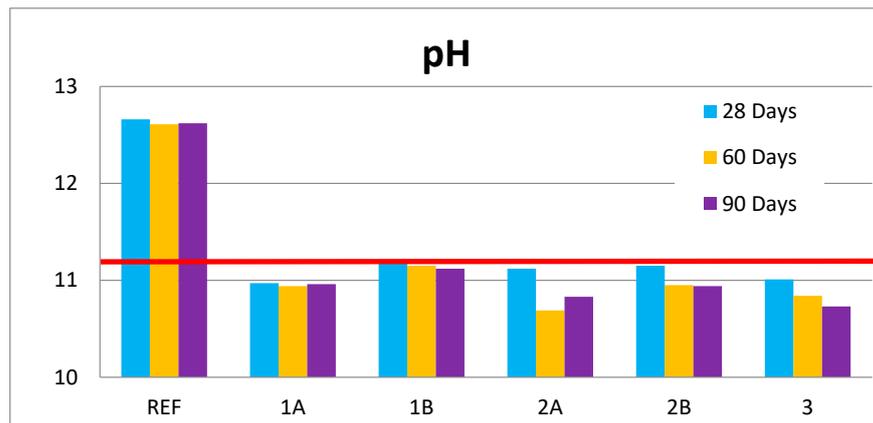


Figure 4. Decrease in pH in concretes dependent on time.

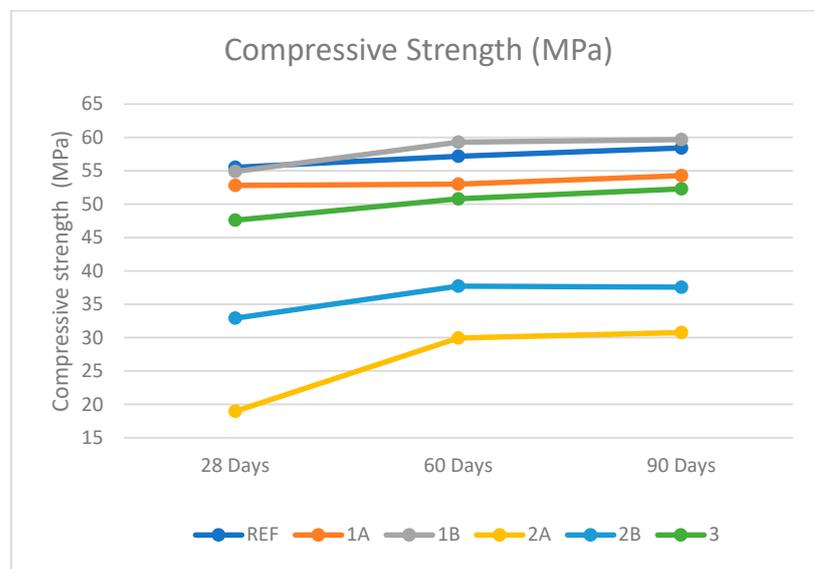


Figure 5. Compressive strength of concrete, measured after 28, 60, and 90 days from mixing.

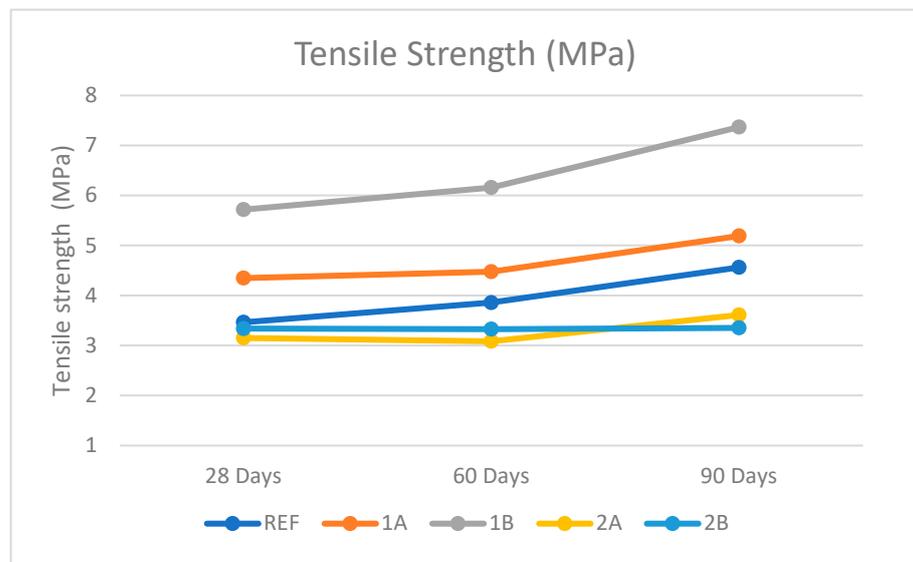


Figure 6. Tensile strength of concrete, measured after 28, 60, and 90 days from mixing.

The modulus of elasticity of concrete does not change much over time. The modulus of elasticity is again higher for samples 1A, 1B, and 3 than for samples 2A and 2B. However, the formulations of samples 1A and 1B were not good due to the poor processability of the fresh mixture. Therefore, mixtures 2A and 2B were mixed, but they could not be used due to the poor properties of fresh mixture and concrete. Mixture 3 was finally optimal—the fresh mix had good processability and the concrete had comparable properties to the reference concrete sample. The results for the modulus of elasticity are summarized in detail in Figure 7.

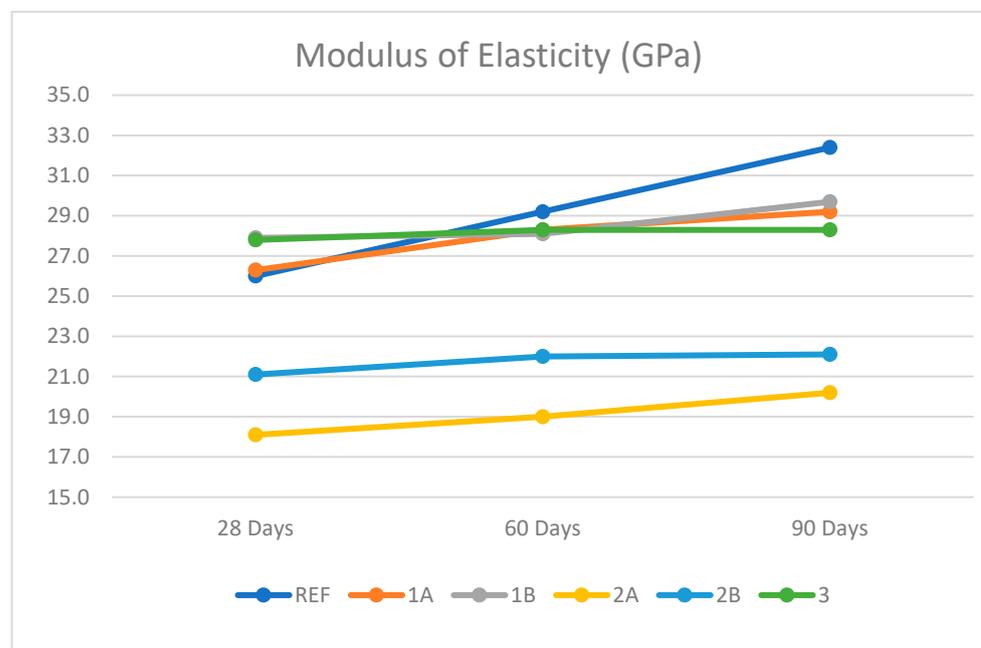


Figure 7. Modulus of elasticity of concrete, measured after 28, 60, and 90 days from mixing.

The shrinkage results of the concrete samples can be seen in the graph in Figure 8. The shrinkage of the reference sample after 90 days was 0.419 mm/m. The shrinkage of the samples from the first formulation (1A, 1B) was about 0.6 mm/m, the shrinkage of sample 2B was 0.405 mm/m, and the shrinkage of sample 2A was 0.893 mm/m. Sample 2A showed higher shrinkage because it contained more water than sample 1A. In contrast,

sample 2B achieved lower shrinkage, although it contained more binder than sample 2A. This is due to the optimization of the individual components of the mixture and the increase in the plasticizer used. The shrinkage was not measured on the final formulation no. 3, as this recipe has the same composition with formulation 2B except for the addition in the form of a defoamer, and a similar shrinkage is therefore assumed.

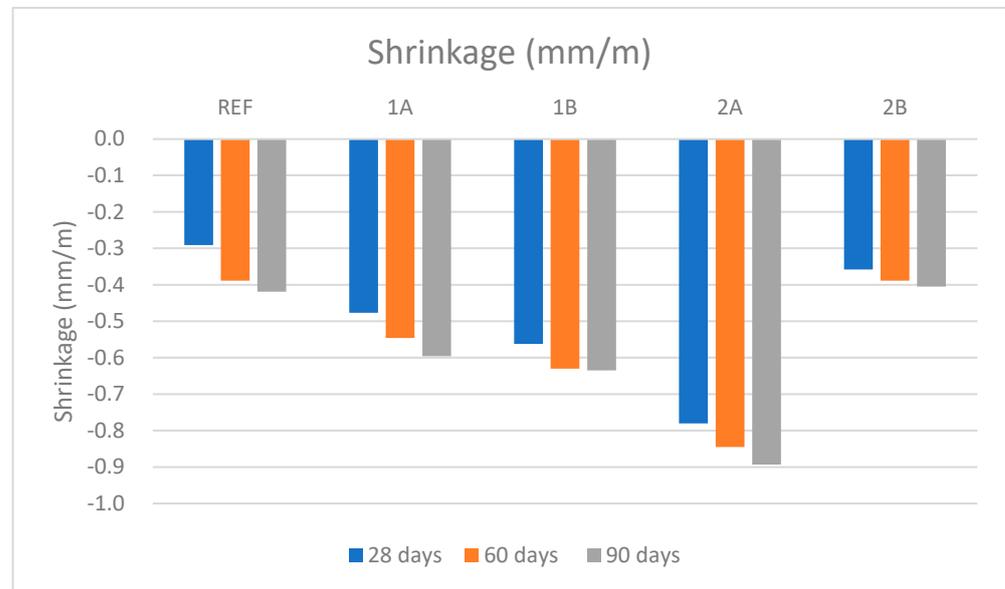


Figure 8. Shrinkage of concrete, measured after 28, 60, and 90 days from mixing.

The absorptivity of concrete was high (5.8–6.5%) in concrete samples 2A and 2B, where there was a high air content, and therefore a high porosity. For samples 1A, 1B, and 3, where the air content in the fresh mixture was in the required range, the absorptivity was between 3.1–3.4%. These numbers are approximately the same as the absorptivity of the concrete reference sample. Results can be seen in the graph in Figure 9.

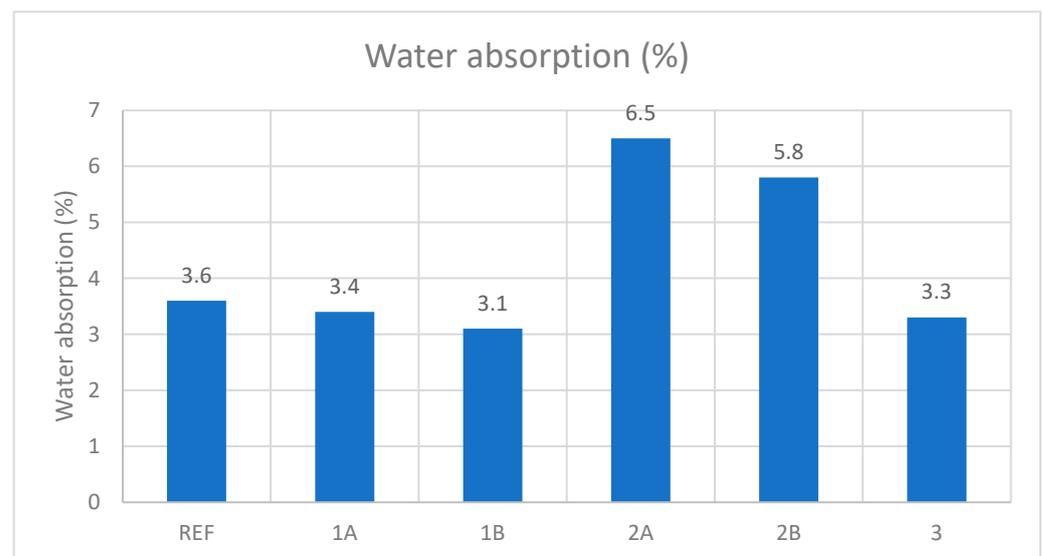


Figure 9. Water absorption of concrete after 28 days from mixing.

The heat during cement hydration measured on concretes was in all cases lower than in the reference sample. The lower the heat generated during cement hydration in massive structures, the more any damage caused by chemical processes and the formation of cracks

on the structure is eliminated. The highest values of temperatures during hydration were reached by sample 1B, namely 37.6 °C. On the contrary, samples 2A and 3 had the lowest, because there was a higher water coefficient w/c than in formulation 2B and a lower proportion of cement. Temperatures for samples 2A and 3 reached 30.3 °C, which is about 30% lower than for the reference sample. The temperatures shown in the graph in Figure 10 were measured after the first 7 days after mixing.

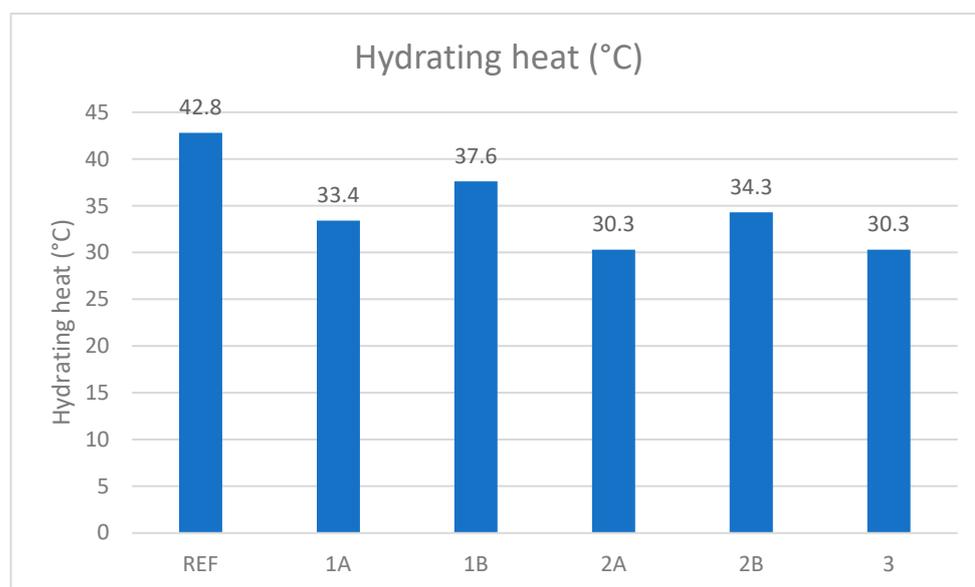


Figure 10. Hydrating heat of concrete after 28 days from mixing.

3.3. Shotcrete

The issue of a sprayed variant of the LPC was solved as well. Due to the requirement for spraying underground, a variant of dry spraying was chosen. In this spraying variant, the dry mixture is supplied under pressure from the filling machine to the hose. At the end of the head, the dry mixture is mixed with water, and where appropriate, with an accelerator in the nozzle. The amount of water in the mixture is regulated according to a visual inspection of the sprayed area (adhesion of the fresh mixture to the underlayer). Therefore, it is not possible to determine the amount of water in the mixture in advance.

The formula of the sprayed mixture was based on a resulting variant 3. Due to the dry spraying method, a variant of the LPC mortar, i.e., a mixture without coarse aggregate, was chosen. The reason for applying the mortar was the necessity of premixing and sacking the dry components of the mixture, and this can only be carried out up to a certain fraction of filler. A continuous supply of coarse aggregate is not possible in the DGR. At the same time, finer and more homogeneous material is more suitable for uneven wall surfaces (rock). Plasticizer and defoamer were excluded from the recipe. This was due to the fact that thorough mixing was necessary to activate the plasticizer. In this case, it would be dispensed into the mixture only in the nozzle, and therefore, due to the high number of fine-grained particles (especially microsilica), there would be insufficient mixing. The mixture with the plasticizer could also run down the wall vertically.

The test injection underground was carried out on the 12th floor of the mine in PVP Bukov. The steel mesh was removed on part of the corridor and the rock was rinsed before being sprayed with water. Spraying is always perpendicular to the surface being sprayed. The water content was optimized during spraying with the device so that the material did not fall off the wall and adhered to the previous layer. The thickness of the coating varied from 5–10 cm depending on the surface roughness. In some cases, a thicker layer was sprayed due to the irregularity and unevenness of the surface. The sprayed mixture created a homogeneous surface, which can be seen in Figure 11.



Figure 11. A view of the applied surfaces with sprayed LPC in the underground.

4. Discussion

At the beginning of this article, it is stated that scientists are trying to solve the question of the possibility of radioactive waste disposal. Bentonite is used as a sealing material, which can be negatively affected by concrete, and therefore scientists are developing concrete with a reduced pH, thus reducing the risk of negatively affecting the bentonite [4,8,12,46].

The article deals with the research of concrete formulations intended for the storage of radioactive waste with a long-term low pH, the value of which should be around 11. However, the resulting concrete must have similar material properties as conventional concrete with CEM I 42.5 cement after 90 days of hardening of the samples. In the initial phase, at the time of mixing the mixtures, all concretes have a similar pH, which, however, decreases over time. The steepness of the drop and its resulting value in the long term depends on the selected binder [47,48]. The main influence is not its total amount, but especially the combination of individual binder components and their chemical composition [16,20,32,49]. The design of the concrete was preceded by an extensive survey on the suitability of the raw materials used.

In a pilot study [31] that preceded this work, cement mortars were designed in a composition that was inspired by recipes from existing work [16,18,19,23,29,32,50]. However, the physical–chemical properties did not achieve satisfactory results. Thus, the proposed formulation per 1 m³ of mixture contains 140 kg of cement, which is about 50% compared to the reference sample, which is in accordance with other studies [16,19,20]. In addition, to improve chemical stability, slag was added to the recipe at 10% to the detriment of OPC [16,36]. Therefore, 60% of the cement is replaced by a binder containing SiO₂. The addition of microsilica or slag as SiO₂-rich components to concrete to achieve low pH is also consistent with the literature [23]. However, such a combination of binder for low pH is quite unique and has not been researched yet. The Ca/Si ratio is 140/211, which is 0.66, and this number is higher than 0.6. The chemically stable concrete should not have a ratio of less than 0.6 according to the literature [16].

Further modification of the formulas depended on the results of tests carried out on the fresh mixtures. The workability of the mixture was tested at first. Recipes marked with number 1 showed very low values of cone sump. In this case, it is necessary to reach

at least the values of consistency that rank to the class S3. Such a requirement results from the assumption of the future application in the form of shotcrete [20]. There was a further modification of the recipes by increasing the water factor. The mixture adjusted in this way already meets the required consistency; however, it has a high air content. This phenomenon is especially bad for the mechanical properties of concrete [11]. Therefore, a defoamer was added.

The process of recipe modification depending on the results of the fresh mixture is illustrated in the form of a flow chart. In an industrial company, only the resulting recipe 3 would be examined further, due to the complexity and difficulty of the measurement. To clarify the development and properties in the article, we dealt with the properties of concrete for all recipes.

Research shows that the pH value of the concrete with a lower pH measured 90 days after mixing should be around 11, so a limit value of 11.2 was chosen [16,19,20,32,49]. At the same time, this concrete should have comparable mechanical properties to conventional concrete containing CEM I 42.5. These characteristics should be achieved after 90 days of hardening of test samples.

As reference, a mixture with a binder:filler ratio of 1:6 was chosen. The resulting values of the compressive strength corresponded to the normal concrete with CEM I 42.5 R cement. In the initial design of the low-pH recipe (formula 1A), OPC was replaced with active ingredients [16,19,20,29,32]. Since it was probably assumed that the strength would not reach the required values due to the large replacement of cement (60%), mixture 1B was created. The binder:filler ratio was changed to 1:4.5 for this recipe. The compressive strength results corresponded to the assumption of the behavior of the addition of microsilica to concrete [51]. The primary goal of adding microsilica to concrete is to increase its strength [52–54], when very fine ground grains of microsilica (approximately 100× smaller than cement) fill the gaps in the matrix and the concrete becomes denser [55,56]. However, when dosing in such a high amount of microsilica, the mixture becomes denser and less workable, and therefore cannot be sufficiently compacted, which is the reason for the decrease in strength [56]. The addition of microsilica to the concrete instead of cement resulted in a reduction in strength by approximately 7% compared to the reference recipe. Mixture 1B with an increased amount of binder already fully corresponds to the values of the reference mixture, and their strength after 90 days varied in the range of several MPa.

In the proposed mixtures 2A and 2B, the water factor was increased due to the workability of the mixture. However, this resulted in the increased porosity of the mixture, and thus a decrease in strength. [57,58]. This phenomenon was also reflected in other measured properties, such as an increase in shrinkage or an almost two-fold increase in water absorption values. This behavior corresponds to the standard behavior of concrete when the water content is changed [11,59]. The final formula, with a defoamer, reduced the porosity of the mixture almost 5 times, to a value of 2.4%. The resulting compressive strength thus approached the values of the reference concrete. The greatest increase in strength took place in the early stages, which was caused by the use of fast-hardening cement CEM I 42.5R, as well as the properties of microsilica itself [58]. The difference in mechanical properties during a time is given by a combination of variance of the tests themselves and the production technology. However, differences in the order of tenths of MPa are due to measurement uncertainties. Similar behavior is also observed for the measured modulus of elasticity and tensile strength.

The recipe designed in this way meets the basic requirements for the mechanical and physical properties of low-pH concrete [16,19,32], and can be further investigated. An interesting measurement would certainly be to determine the size and distribution of the pores in the hardened structure due to its diffusion properties, which strongly influence the processes taking place at the concrete/bentonite interface [12–14,60,61].

5. Conclusions

Developing low-pH concrete is a complex issue, which includes various aspects influencing the physical–chemical properties of mixtures. From the results of this work, the following can be concluded:

- A controlling factor for designing an LPC is the characteristics of the fresh mixture. The processability of the mixture (with regard to its further use) plays a significant role in deciding on the type and quantity of additives.
- The results of mechanical tests show a similar value as normal concrete (CEM I 42.5) and at the same time meet the required value of pH for low-pH concretes (in this case, a pH value of around 11 in the long term).
- The final designed recipe has a different binder composition (CEM I 40%, microsilica 51%, and slag 9%) than was presented in previous studies in previous years. This is due to the use of local raw materials. It is assumed that one cannot simply adopt the formula of LPC without checking its properties.
- Due to application of low-pH shotcrete, it was proved that the designed mixture can be modified for the technology of sprayed concrete, even for use under the ground.

The scientific work described in this article is followed by an expert study of long-term monitoring of produced samples from the final formulation 3. The samples were stored in a place corresponding to the conditions of the presumed radioactive waste repository, and their chemical–physical properties will be monitored over the following years.

Author Contributions: Formal analysis, D.D. and T.M.; investigation, D.D. and T.M.; methodology, R.P. and D.C.; project administration, D.C.; supervision, L.H.; writing—original draft, R.P.; writing—review and editing, J.K. and L.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research is supported by Radioactive Waste Repository Authority—SÚRAO under project No. SO2017-094 and also has been funded by the institutional support for the development of the research organization, Klokner Institute of the Czech Technical University in Prague.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article material.

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

References

1. El-Showk, S. Final resting place. *Science* **2022**, *375*, 806–810. [CrossRef]
2. Keusen, H.R.; Ganguin, J.; Schuler, P.; Buletti, M. *Grimmel Test Site: Geology*; Nationale Genossenschaft fuer die Lagerung Radioaktiver Abfaelle: Wettingen, Switzerland, 1989; pp. 1–167.
3. Tournassat, C.; Steefel, C.I.; Bourg, I.C.; Bergaya, F. Natural and Engineered Clay Barriers. In *Developments in Clay Science*; Elsevier: Amsterdam, The Netherlands, 2015; pp. 1–4.
4. Stastka, J.; Hanusova, I.; Hausmannova, L.; Kucerova, M. In-situ testing of Czech bentonite for radioactive waste disposal in Mock-up Josef experiment. *Ann. Nucl. Energy* **2022**, *172*, 109059. [CrossRef]
5. SÚRAO. Available online: <https://www.surao.cz/ke-stazeni/> (accessed on 16 June 2022).
6. Špinka, O.; Grunwald, L.; Zahradník, O.; Veverka, A.; Fiedler, F.; Nohejl, J. *Siting Study—Březový Potok*; Final report 139/2017; SÚRAO: Prague, Czech Republic, 2018.
7. Kotnour, P. *Výzkum a Vývoj Ukládacího Obalového Souboru Pro Hlubinné Ukládání Vyhořelého Jaderného Palíva Do Stádia Realizace Vzorku 3. Etapa*; Technical report; SÚRAO: Prague, Czech Republic, 2017.
8. Smutek, J.; Hausmannova, L.; Svoboda, J. The gas permeability, breakthrough behaviour and re-sealing ability of Czech Ca-Mg bentonite. *Geol. Soc. Spec. Publ.* **2017**, *443*, 333–348. [CrossRef]
9. Hausmannová, L.; Hanusová, I.; Dohnálková, M. *Summary of the Research of Czech Bentonites for Use in the Deep Geological Repository—Up to 2018*; Technical report 309/2018/ENG; SÚRAO: Prague, Czech Republic, 2018.
10. Malmgren, L.; Nordlund, E.; Rolund, S. Adhesion strength and shrinkage of shotcrete. *Tunn. Undergr. Space Technol.* **2005**, *20*, 33–48. [CrossRef]
11. Collepardi, M. *The New Concrete*; Tintoretto: Los Angeles, CA, USA, 2006; pp. 1–241.
12. Svoboda, J.; Mašín, D.; Najser, J.; Vašíček, R.; Hanusová, I.; Hausmannová, L. BCV bentonite hydromechanical behaviour and modelling. *Acta Geotech.* **2022**, *297*, 1–19. [CrossRef]

13. Savage, D. *An Assessment of the Impact of the Long Term Evolution of Engineered Structures on the Safety Relevant Functions of the Bentonite Buffer in a HLW Repository*; National Cooperative for the Disposal of Radioactive Waste: Wettingen, Switzerland, 2014.
14. Gaboreau, S.; Pret, D.; Montouillout, V.; Henocq, P. Quantitative mineralogical mapping of hydrated low pH concrete. *Cem. Concr. Compos.* **2017**, *83*, 360–373. [[CrossRef](#)]
15. Lerouge, C.; Gaboreau, S.; Grangeon, S.; Claret, F.; Warmont, F.; Jenni, A.; Cloet, V.; Mäder, U. In situ interactions between Opalinus Clay and Low Alkali Concrete. *Phys. Chem. Earth Parts A/B/C* **2017**, *99*, 3–21. [[CrossRef](#)]
16. Vehmas, T.; Holt, E. *WP1 Experimental Studies—State of the Art Literature—Review*; CEBAMA, European Union: Imperatriz, Brazil, 2016; pp. 1–235.
17. Mohammed, M.H.; Pusch, R.; Knutsson, S.; Warr, L.N. Hydrothermal alteration of clay and low pH concrete applicable to deep borehole disposal of high-level radioactive waste—A pilot study. *Constr. Build. Mater.* **2016**, *104*, 1–8. [[CrossRef](#)]
18. García Calvo, J.L.; Hidalgo, A.; Alonso, C.; Fernández Luco, L. Development of low-pH cementitious materials for HLRW repositories. Resistance against ground waters aggression. *Cem. Concr. Res.* **2010**, *40*, 1290–1297. [[CrossRef](#)]
19. Leivo, M.; Holt, E.; Vehmas, T. *Betonirakenteet Ydinpolttoaineen Loppusijoituksessa*; Teknologian Tutkimuskeskus VTT: Espoo, Finland, 2013; pp. 1–21.
20. Vogt, C.; Lagerblad, B.; Wallin, K.; Baldy, F.; Jonasson, J.E. *Low pH Self-Compacting Concrete for Deposition Tunnel Plugs*; Report R-09-07; Swedish Nuclear Fuel and Waste Management: Stockholm, Sweden, 2019; pp. 1–78.
21. Zuo, J.; Zhan, J.; Dong, B.; Luo, C.; Liu, Q.; Chen, D. Preparation of metal hydroxide microcapsules and the effect on pH value of concrete. *Constr. Build. Mater.* **2017**, *155*, 323–331. [[CrossRef](#)]
22. Nishimura, T.; Raman, V. Corrosion behavior of reinforcing steel in concrete for nuclear facilities exposed in high chloride and low pH environment. *J. Nucl. Mater.* **2010**, *397*, 101–108. [[CrossRef](#)]
23. El Bitouri, Y.; Buffo-Lacarrière, L.; Sellier, A.; Bourbon, X. Modelling of chemo-mechanical behaviour of low pH concretes. *Cem. Concr. Res.* **2016**, *81*, 70–80. [[CrossRef](#)]
24. Prošek, Z.; Nežerka, V.; Hlůžek, R.; Trejbal, J.; Tesárek, P.; Karra'a, G. Role of lime, fly ash, and slag in cement pastes containing recycled concrete fines. *Constr. Build. Mater.* **2019**, *201*, 702–714. [[CrossRef](#)]
25. Pernicova, R.; Pavlikova, M.; Cerny, R. Effect of metakaolin on chloride binding in lime-based composites. In *Computational Methods and Experimental Measurements XIII*; WIT Press: Boston, MA, USA, 2007; Volume 46, p. 357.
26. Hoškova, S.; Tichá, P.; Demo, P. Determination of Ca²⁺ ions at early stage of hydrating cement paste fines. *Ceram.-Silik.* **2009**, *53*, 76–80.
27. Cong, X.; Kirkpatrick, J.R. ²⁹Si MAS NMR study of the structure of calcium silicate hydrate. *Adv. Cem. Based Mater.* **1996**, *3*, 144–156. [[CrossRef](#)]
28. Hong, S.Y.; Glasser, F.P. Alkali binding in cement pastes Part I. The C–S–H ph. *Cem. Concr. Res.* **1999**, *29*, 893–1903. [[CrossRef](#)]
29. Dole, L.R.; Mattus, C.H. Low pH Concrete for use in the high-level waste repository: Part I overview. In *R&D on Low-pH Cement for a Geological Repository*; Nuclear Science Technology Division of Oak Ridge National Laboratory: Oak Ridge, TN, USA, 2007.
30. Bellmann, F.; Erfurt, W.; Ludwig, H.M. Field performance of concrete exposed to sulphate and low pH conditions from natural and industrial sources. *Cem. Concr. Compos.* **2012**, *34*, 86–93. [[CrossRef](#)]
31. Pernicová, R.; Čítek, D.; Dobiáš, D.; Kolísko, J.; Mandlík, T.; Hausmannová, L. Effect of Binder Components on the pH of Concrete Mixture with Low pH Intended for Deep Geological Repository for Radioactive Waste in the Czech Republic. *Key Eng. Mater.* **2020**, *868*, 15–23. [[CrossRef](#)]
32. Coumes, C.D. *Low pH Cements for Waste Repositories: A Review*; Laboratoire d'Etude de l'Enrobage des Déchets: Marcoule, France, 2008; pp. 1–42.
33. Hlaváč, J. *Základy Technologie Silikátů*, 2nd ed.; SNTL: Praha, Czech Republic, 1988; pp. 444–465.
34. Klecka, T. *Příručka Technologa—BETON*, 2nd ed.; HeidelbergCement: Beroun, Czech Republic, 2005; pp. 1–292.
35. Silica Fume Association. What Is Silica Fume? Available online: <https://www.silicafume.org/general-silicafume.html> (accessed on 4 August 2022).
36. Bilim, C.; Atiş, C.D.; Tanyildizi, H.; Karahan, O. Predicting the compressive strength of ground granulated blast furnace slag concrete using artificial neural network. *Adv. Eng. Softw.* **2009**, *40*, 334–340. [[CrossRef](#)]
37. MCT—Betonové Výrobky a Beton. Available online: <https://www.mct.cz/> (accessed on 16 June 2022).
38. ČSN EN 12350-6; Testing Fresh Concrete—Part 6: Volumetric Mass Density. European Committee for Standardization: Brussels, Belgium, 2020.
39. ČSN EN 12350-7; Testing Fresh Concrete—Part 7: Air Content—Pressure Methods. European Committee for Standardization: Brussels, Belgium, 2020.
40. ČSN EN 12390-7; Testing Hardened Concrete—Part 7: Density of Hardened Concrete. European Committee for Standardization: Brussels, Belgium, 2020.
41. Behnood, A.; van Tittelboom, K.; de Belie, N. Methods for Measuring pH in Concrete: A review. *Constr. Build. Mater.* **2016**, *105*, 176–188. [[CrossRef](#)]
42. ČSN EN 12390-3; Testing Hardened Concrete—Part 3: Compressive Strength of Test Specimens. European Committee for Standardization: Brussels, Belgium, 2020.
43. ČSN EN 12390-5; Testing Hardened Concrete—Part 5: Flexural Strength of Test Specimens. European Committee for Standardization: Brussels, Belgium, 2020.

44. ČSN ISO 1920-10; Testing of Concrete—Part 10: Determination of the Static Modulus of Elasticity in Compression. European Committee for Standardization: Geneva, Switzerland, 2016.
45. ČSN 73 1316; Stanovení Vlhkosti, Nasákavosti a Vzlínivosti Betonu. Czechoslovak State Standard: Prague, Czech Republic, 1990.
46. Dauzères, A.; Achiedo, G.; Nied, D.; Bernard, E.; Alahrache, S.; Lothenbach, B. Magnesium perturbation in low-pH concretes placed in clayey environment—Solid characterizations and modelling. *Cem. Concr. Res.* **2016**, *79*, pp. 137–150. [[CrossRef](#)]
47. Deschner, F.; Winnefeld, B.; Lothenbach, B.; Seufert, S.; Schwesig, P.; Dittrich, S.; Goetz-Neunhoeffler, F.; Neubauer, J. Hydration of Portland cement with high replacement by siliceous fly ash. *Cem. Concr. Res.* **2012**, *42*, 1389–1400. [[CrossRef](#)]
48. Nuclear Decommissioning Authority. *Geological Disposal: Near-Field Evolution Status Report*; Report no. NDA/RWMD/033; Nuclear Decommissioning Authority: England, UK, 2010.
49. Zhang, T.; Cheeseman, C.R.; Vandeperre, L.J. Development of low-pH cementitious materials for HLRW repositories Resistance against ground waters aggression. *Cem. Concr. Res.* **2011**, *41*, 439–442. [[CrossRef](#)]
50. Dauzères, A.; Le Bescop, P.; Sardini, P.; Cau Dit Coumes, C. Physico-chemical investigation of clayey/cement-based materials interaction in the context of geological waste disposal: Experimental approach and results. *Cem. Concr. Res.* **2010**, *40*, 1327–1340. [[CrossRef](#)]
51. Taylor, H.F.W. *Cement Chemistry*; Academic Press: London, UK, 1990; pp. 305–307, 374–378.
52. Behnood, A.; Ziari, H. Effects of silica fume addition and water to cement ratio on the properties of high-strength concrete after exposure to high temperatures. *Cem. Concr. Compos.* **2008**, *30*, 106–112. [[CrossRef](#)]
53. Qing, Y.; Zenan, Z.; Deyu, K.; Rongshen, C. Influence of nano-SiO₂ addition on properties of hardened cement paste as compared with silica fume. *Construct. Build. Mater.* **2007**, *21*, 539–545. [[CrossRef](#)]
54. Mazloom, M.; Ramezaniapour, A.A.; Brooks, J.J. Effect of silica fume on mechanical properties of high-strength concrete. *Cem. Concr. Compos.* **2004**, *26*, 347–357. [[CrossRef](#)]
55. Jeong, Y.; Kang, S.H.; Kim, M.O.; Moon, J. Acceleration of cement hydration from supplementary cementitious materials: Performance comparison between silica fume and hydrophobic silica. *Cem. Concr. Compos.* **2020**, *112*, 103688. [[CrossRef](#)]
56. Khayat, K.H.; Aitcin, P.C. Silica fume: A unique supplementary cementitious material. *Miner. Admix. Cem. Concr.* **1993**, *4*, 227–265.
57. Siddique, R. Utilization of silica fume in concrete: Review of hardened properties. *Resour. Conserv. Recycl.* **2011**, *55*, 923–932. [[CrossRef](#)]
58. Ghafari, E.; Costa, H.; Júlio, E.; Portugal, A.; Durães, L. The effect of nanosilica addition on flowability, strength and transport properties of ultra high performance concrete. *Mater. Des.* **2014**, *59*, 1–9. [[CrossRef](#)]
59. Jia, Y.; Zhao, X.; Bian, H.; Wang, W.; Shao, J.F. Numerical modelling the influence of water content on the mechanical behaviour of concrete under high confining pressures. *Mech. Res. Commun.* **2022**, *119*, 103819. [[CrossRef](#)]
60. González-Santamaría, D.E.; Fernández, R.; Ruiz, A.I.; Ortega, A.; Cuevas, J. High-pH/low pH ordinary Portland cement mortars impacts on compacted bentonite surfaces: Application to clay barriers performance. *Appl. Clay Sci.* **2020**, *193*, 105672. [[CrossRef](#)]
61. Laloui, L.; Ferrari, A.; Bosch, J.A. Bentonite clay barriers innuclear waste repositories. In Proceedings of the 2nd International Conference on Energy Geotechnics (ICEGT 2020), EDP Sciences, La Jolla, CA, USA, 20–23 September 2020; p. 205.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.