Mechanical and thermal properties of concrete suitable for radioactive waste disposal sites

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Abstract. Secondary casing as a part of a multi-barrier system serves to meet the safety requirements on the radioactive waste repositories. Such casing needs to be durable, radiation- and thermal resistant, with good mechanical properties; these requirements are fulfilled by concrete. However, the casing should also serve as a barrier limiting the leaching of radionuclides, in case of failure of primary package. This problem is addressed in the article by the addition of a sorption material (natural zeolite rock) in the concrete mixture. Mechanical and thermal properties of concrete containing different amount of natural zeolite rock are studied with the link to concrete porosity. The addition of natural zeolite is found to cause a decrease in thermal conductivity and specific heat capacity. Both compressive and flexural strength decrease as well when natural zeolite is added in the mixture, which correlates with the increase of open porosity of studied concrete mixtures.

1. Introduction
Radioactive waste repositories require a multi-barrier system of protection to ensure safety of any living species within the repository neighborhood and to preserve the surrounding environment. Such a hazardous waste has to be encapsulated in a solid and durable matrix (cementitious, glass, ceramics etc.) placed in a durable container (usually metal) – this serves as the first protection and it is called a primary package. Primary packages are further protected by secondary engineering barriers, which should further limit the leaching of radionuclides into the final protection barrier, which is comprised by the surrounding rock [1]. However, the last barrier is in direct contact with groundwater, which cannot be contaminated; in that case, the radionuclides would spread in a large environmental area.

For low and intermediate level waste, the secondary barriers are made of concrete for its mechanical properties, durability, low corrosion and low cost. The secondary casing is usually reinforced to have sufficient mechanical parameters in order to withstand the transport, manipulation on site and ground pressure after the final emplacement in the repository [2,3]. Besides the mechanical properties, there are requirements on the radiation stability of concrete, its thermal stability and resistance to aggressive water and eventual organisms. Moreover, the concrete barrier should limit the leaching of radionuclides into the environment in case there is an accidental leak from the primary package. Well known sorption materials for radionuclides such as $^{137}$Cs or $^{90}$Sr etc. are zeolites, both natural or synthetic [4,5]. As zeolites present pozzolanic activity, these can be used as additive in...
concrete taking part in the cement hydration and/or it can act as a filler [6,7]. The article aims at studying the properties of concrete incorporating natural zeolite as an additive to enhance the sorption properties of secondary casing in rad-waste repositories. The paper is focused on the change in mechanical and thermal properties of concrete when different amount of zeolite is added in the concrete mixture.

2. Materials and methods

2.1. Materials

Table 1 presents the composition of studied materials. The concrete mixtures were designed to have high strength with continuous granulometry curve made of three fractions of aggregates Dobříň (Quartz, Spar) and Zbraslav (Andezite) complemented with fine filler – silicate flour ST6 (specific surface – 0.4 m²g⁻¹, d50 = 16 µm). The principal binder component was Portland cement CEM I 42.5 R, which was the only binder component for the reference mixture RZR. In the next four mixtures, natural zeolite rock was added in different amounts. 10% of cement weight (40 kg in 1 m³) was substituted by natural zeolite (ZeoBau 200, specific surface – 24.5 m²g⁻¹, d50 = 34 µm), which takes part in the hydration of the binder system, then the addition of zeolite was dosed increasingly by 40 kg m⁻³, while the cement dosage was kept constant and zeolite rock served as an inert mineral additive. Superplasticizer Stachement 2000 (based on polycarboxylate) was added to achieve good rheology of the fresh mixture and the amount of water was dosed in order to meet the prescribed slump of the fresh mixture. Table 2 gives the chemical composition of the input materials.

| Table 1. Composition of studied materials. |
|--------------------------------------------|
|                                           |
| RZR | RZ1 | RZ2 | RZ3 | RZ4 |
| Portland cement CEM 42.5 R [kg/m³] | 400 | 320 | 320 | 320 | 320.00 |
| Natural zeolite ZeoBau 200 [kg/m³] | 80  | 120 | 160 | 200 |
| Silicate flour ST6 [kg/m³]  | 120 | 120 | 80  | 40  | -     |
| Aggregates 0-4 mm Dobříň [kg/m³] | 760 | 760 | 760 | 760 | 760   |
| Aggregates 4-8 mm Zbraslav [kg/m³] | 455 | 455 | 455 | 455 | 455   |
| Aggregates 8-16 mm Zbraslav [kg/m³] | 483 | 483 | 483 | 483 | 483   |
| Superplasticizer - Stachement 2000 [kg/m³] | 6.9 | 6.9 | 6.9 | 6.9 | 6.9   |
| Water [kg/m³] | 195 | 160 | 160 | 160 | 160 |

| Table 2. Chemical composition of the input materials (wt. %). |
|-------------------------------------------------------------|
| Portland cement 42.5 R | Natural zeolite | Silicate flour |
| SiO₂  | 18.7 | 74.5 | 99.7 |
| Al₂O₃ | 4.5  | 15.4 | 0.2  |
| Fe₂O₃ | 3.4  | 1.6  | -    |
| CaO   | 65.9 | 3.3  | -    |
| MgO   | 1.3  | 0.7  | -    |
| K₂O   | 0.8  | 3.5  | -    |
| Na₂O  | 0.2  | 0.6  | -    |
| TiO₂  | 0.3  | 0.2  | -    |
| SO₃   | 4.3  | 4.9  | -    |
| P₂O₅  | 0.1  | 0.2  | -    |
2.2. Experimental methods

2.2.1. Basic physical properties. Bulk density, \( \rho \) [kg·m\(^{-3}\)], matrix density, \( \rho_{\text{mat}} \) [kg·m\(^{-3}\)], and open porosity \( \psi \) [%] were measured using the helium pycnometry (Pycnomatic ATC) and water vacuum saturation method [8].

For the determination of the pore distribution, mercury intrusion porosimetry was used. The experiment was carried out by Pascal 140 and Pascal 440 devices. Results were plotted as the cumulative curves of pore specific volume in dependence on the pore diameter and distribution curves of incremental pore volumes in dependence on the pore diameter.

2.2.2. Mechanical properties. Compressive strength [MPa] and flexural strength [MPa] as the main mechanical parameters were determined according to CSN EN 12390-3 [9] and CSN EN 12390-5 [10] respectively; device EU 40 was used. The strength was determined for 28-days cured samples.

2.2.3. Thermal properties. The thermal conductivity, \( \lambda \) [W·m\(^{-1}\)·K\(^{-1}\)], and the specific heat capacity, \( c \) [J·kg\(^{-1}\)·K\(^{-1}\)], in dependence on the weight fraction of water in the material, were determined to assess the thermal properties. The pulse method was used with the use of portable device ISOMET 2114.

3. Results and discussion

3.1. Basic physical properties

Measured parameters of basic physical properties are given in table 3. Results obtained by pycnometry and gravimetric method correlated well with the results gained from vacuum saturation, only in a little bit higher absolute values. Bulk density as well as matrix density decreased with the increasing amount of zeolite in the mixture, which is the result of increasing open porosity. This is caused by the very porous nature of the input zeolite with channels of pores. The decrease of bulk and matrix density is within 15%, which is insignificant, but the increase in open porosity is by 45% when comparing RZ4 with the reference mixture. However, the increasing trend is not proportional as there is high rise in values for RZ1 compared to RZR (by 37%), but the further increase is lower. This means that even the initial 10% of natural zeolite which should have taken part in the pozzolanic reaction, resulted in increase of porosity of the hardened structure of concrete.

Table 3. Basic physical properties of studied materials.

|                | Water vacuum saturation method | Pycnometry and gravimetric method |
|----------------|--------------------------------|-----------------------------------|
|                | Bulk density [kgm\(^{-3}\)]   | Matrix density [kgm\(^{-3}\)]     | Open porosity [%]                 |
|                |                                |                                  | Bulk density [kgm\(^{-3}\)]      | Matrix density [kgm\(^{-3}\)] | Open porosity [%] |
| RZR            | 2 319                          | 2 579                            | 10.1                              | 2 361                          | 2 638 | 10.5 |
| RZ1            | 2 111                          | 2 514                            | 16.0                              | 2 166                          | 2 595 | 16.5 |
| RZ2            | 2 097                          | 2 505                            | 16.3                              | 2 157                          | 2 594 | 16.8 |
| RZ3            | 2 046                          | 2 456                            | 16.7                              | 2 152                          | 2 595 | 17.1 |
| RZ4            | 2 002                          | 2 448                            | 18.2                              | 2 082                          | 2 606 | 20.1 |

Figures 1 and 2 present the pore size distribution. It can be seen that there is higher amount of larger pores (sizes around 10 - 100 µm) for the reference mixture in comparison to RZ1 and RZ2. However, the total pore volume is lower in case of RZR. For RZ3 and RZ4 there are higher amounts of all sizes of pores. It can be concluded that the presence of natural zeolite increases the total
porosity, but there is a shift in the average size of pores from macro-pores (10 – 100 µm) to micro-pores (around 0.1 µm).

Figure 1. Cumulative curve of pore size distribution of studied materials.

Figure 2. Pore size distribution curves of studied materials.

3.2. Mechanical properties

Results of mechanical properties are given in table 4. There is a clear decreasing trend for both compressive and flexural strength. The drop of compressive strength for RZ1 compared to reference concrete is by 35% and in case of RZ4 the residual strength is at about half the reference value. In case of flexural strength, the decrease for RZ1 is lower than in case of compressive strength – “only” by
12%; but for RZ4 again the flexural strength showed only half the reference value. The results correlate well with the values of measured porosities, which indicates that the worsened mechanical properties were caused by the increase in open porosity.

**Table 4. Mechanical properties of studied materials.**

| Material | Compressive strength [MPa] | Bending strength [MPa] |
|----------|----------------------------|------------------------|
| RZR      | 165.73                     | 8.04                   |
| RZ1      | 107.67                     | 7.06                   |
| RZ2      | 101.73                     | 6.02                   |
| RZ3      | 87.50                      | 4.31                   |
| RZ4      | 85.75                      | 4.17                   |

### 3.3. Thermal properties

Figures 3 and 4 present the values of measured thermal properties in dry and saturated state. There is a decrease of thermal conductivity of concrete when natural zeolite is present. The drop is for RZ1 in comparison to reference mixture is by 30% and 23% for dry and saturated state respectively, however further decrease with increasing amount of zeolite is negligible in both dry and saturated state. The only exception is RZ4, where a further drop in the dry state by 15% was recorded.

Values of specific heat capacity in the dry state of RZ4 concrete were 40% below the reference. A decreasing trend was recorded also for the saturated state, however the rate of the decline was lower, as the value of RZ4 decreased “only” by 20% in comparison to the reference concrete.

**Figure 3. Thermal conductivity of studied materials.**
4. Conclusions
The need to ensure safety criteria within the radioactive waste repositories calls for finding the best way how to limit any leaching of radionuclides into the environment. Although this is the main task of primary packages in the multi-barrier system of the rad-waste repository, it is always better to have double protection. Therefore, there is ongoing research on studying concrete for secondary engineering barrier incorporating natural zeolite as a good sorbent of radionuclides. The paper studied the mechanical and thermal properties in connection to the porous system. However, despite the good sorption properties of natural zeolite, its presence in concrete for secondary barriers result in significant worsening of mechanical properties due to increased porosity. And also in the view of thermal properties, the thermal conductivity and specific heat capacity decreased with the incorporation of natural zeolite. Further experiments and numerical simulations need to be made to consider the advantages and disadvantages of the zeolite presence in secondary barrier concrete.

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