Pore structure and hygric properties of composite materials for radionuclide protection barriers

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Abstract. Many practical applications of concrete require adjustment of its properties. If concrete is used as casing for radioactive waste deposits, its main purpose is to mitigate radionuclide release and the mix design must conform to this requirement. In this article bentonite as a material with great sorption capacity is used as a concrete component. The main issue is to assess durability of designed mixtures. Therefore, the pore structure and hygric properties are investigated. The experimental results show that bentonite utilization in concrete mixtures leads to a significant growth of pore amount in the range of 0.01 to 1 μm and increase of water transport ability.

1 Introduction

The global energy consumption has been rapidly growing; by about 10 million gigawatts in last decades. Unfortunately, current demands cannot be satisfied by conventional sources, such as fossil fuels (coal, petroleum, or natural gas), not even by renewables. Nuclear power could serve, if not as a permanent great source of energy, then as a temporary source, as long as another functional source capable to satisfy current demands will be found. However, its great disadvantage is a production of radioactive waste. Management of waste disposal is a difficult issue to be addressed [1]. It covers many accurate requirements and regulations, which have to be fulfilled in order to prevent radioactive substances release. Nowadays the most utilized solution is creation of deposits, where waste can be stored until its decomposition to safe nuclides, or up to development of new technology for radioactive waste elimination. One of the most common kinds of barrier in repositories is concrete casing [2, 3]. Except for superior durability those concrete have to serve as radioactive protection and they should mitigate a radionuclide release [4]. The radionuclides transport can be inhibited by incorporation of some sorption materials in to the concrete mixture. For that reason natural clays or synthetic alternatives [5, 6, 7, 8] were successfully used.

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In this study, bentonite is used as sorption admixture in concrete. High sorption capacity, high cation exchange value, swelling and plasticity ability belong among its characteristic properties. Several mixtures containing this natural clay are investigated, and concrete durability is assessed using basic physical and hygric properties.

2 Studied materials

Several mixtures with varying amount of bentonite were designed (Table 1). The reference material was labeled as RBR and it was based on Portland cement and did not contain bentonite. It was believed that bentonite could take part in the pozzolanic reaction. Therefore, 20% of cement was replaced by bentonite in all other mixtures. However, the main role of bentonite should be as a sorption admixture, so in some other mixes it was used as a replacement of silica flour.

Table 1. Material composition of studied concretes (kg m⁻³)

Component	RBR	RB1	RB2	RB3	RB4
Portland cement	400	320	320	320	320
Bentonite	-	80	120	160	200
Silica flour	120	120	80	40	-
Aggregates 0-4 mm	760	760	760	760	760
Aggregates 4-8 mm	455	455	455	455	455
Aggregates 8-16 mm	483	483	483	483	483
Superplasticizer	6.9	6.9	6.9	6.9	6.9
Water	195	165	160	160	160

Fig. 1. Particle size distribution of cement, bentonite and silica flour

The applied sodium bentonite B75 (produced by Keramost a.s., Most) contained 65% to 85% of montmorillonite and up to 7% of sodium carbonate. Its density was 2600 kg m⁻³, its particle size distribution curves determined using a laser diffraction analyzer (Fritsch, Analysette 22 MicroTec plus) are presented in Figure 1 together with the other raw materials. As a binder, Portland cement CEM I 42.5 R (produced by Českomoravský cement, a.s., Mokrý) was chosen, having a specific surface of 408 m² kg⁻¹. The reference fine admixture was silica flour ST6 (originate in Sklopisek Střeleč a.s.). Its density was

2650 kg m⁻³. Three aggregate gradings were used, specifically 0-4 mm grade of silica sand (CEMEX Czech Republic, s.r.o., gravel-pit Dobřín) and 4-8 mm and 8-16 mm grades of rock mixture (both from KÁMEN Zbraslav, a.s., Zbraslav). For a better workability superplasticizer Stachement 2000 (STACHEMA CZ s.r.o.) based on polycarboxylates was used. The last component was portable water, dosed in different amount, so the fresh mixtures reached the same consistency.

3 Experimental methods, results and discussion

3.1 Basic physical properties

The matrix density was determined by helium pycnometry. This experiment was carried out using the device “Pycnomatic ATC” from Thermo Fisher Scientific Inc. This device has analogous principle as a common pycnometry, but the medium for volume determination is not water but gas, which is expected to fill even very small pores (due to the small dimension of helium molecules). The volume of studied material is determined by virtue of measurement of gas pressure in a chamber and using the Boyle-Marriott law. Bulk density was determined by the gravimetric method. Three cubic samples with the edge of 50 mm were dried in a drying box at the temperature of 105 °C, then their mass and exact dimensions were determined. The open porosity was calculated from the values of matrix density and bulk density.

The obtained values of basic physical properties are summarized in Table 2. Regarding the matrix density, these values were almost equal. The difference was less than 2%, in accordance with the accuracy of measurement. Thus it could be concluded, that bentonite application had no significant influence on the matrix density of concrete. However, when focused on bulk density, the impact was much more obvious. Due to the bentonite utilization, the bulk densities went down gradually by 12% to 21% with growing amount of bentonite in the mixture. The open porosity was two times higher when bentonite was used as a cement replacement, and further growth was observed when it was used as an admixture.

Table 2. Basic physical properties of studied concretes

	Matrix density[kg m ⁻³]	Bulk density [kg m ⁻³]	Open porosity [%]
RBR	2638 ± 42	2361 ± 31	10.5 ± 1.1
RB1	2594 ± 43	2068 ± 38	20.3 ± 0.9
RB2	2615 ± 31	1980 ± 26	24.3 ± 1.4
RB3	2630 ± 25	1921 ± 19	27.0 ± 1.5
RB4	2635 ± 38	1869 ± 27	29.1 ± 0.8

Characterization of the pore structure was done by mercury intrusion porosimetry. This method consists in measuring the external pressure needed to force the mercury into a pore against the opposing force of the liquid’s surface tension. The pore size is then calculated from the measured pressure using Washburn’s equation. The experiments were carried out using instruments “PASCAL 140 + 440” made by Thermo Fisher Scientific Inc. The range of applied pressure corresponded to the pore radii from 10 nm to 100 μm.

Figure 2 shows the pore size distribution curves of studied concretes. It is obvious that the utilization of bentonite had a significant impact in the range of smaller pores from 0.01 to 1 μm, while bigger pores were not affected. The replacement of cement had a comparable effect on pore size distribution as the replacement of silica flour, which was

similar to the effect of bentonite on the total pore volume. Apparently, the high increase of the amount of pores with a diameter of 0.01 to 1 μm significantly increased the sorption capacity of concretes containing bentonite which enhanced their capability of radionuclide fixation.

Fig. 2. Pore size distribution curves of studied concretes

3.2 Hygric parameters

Water absorption experiment was conducted to characterize the liquid water transport properties. Five samples of dimensions 50 x 50 x 50 mm were covered by epoxy resin on lateral sides to ensure one dimensional water intake. Their bottom sides were immersed by about 2 mm under the water level. The weight changes in dependence on time were continuously recorded and then plotted in a graph. The tangent of the rising part of the plotted curve defined the water absorption coefficient and the apparent moisture diffusivity was then calculated according to [9, 10].

Table 3. Liquid water transport parameters of studied concretes

	Water absorption coefficient [kg m ⁻² s ^{-1/2}]	Apparent moisture diffusivity [m ² s ⁻¹]
RBR	0.0095 ± 0.0004	5.93E-09 ± 2.9E-10
RB1	0.0341 ± 0.0020	3.08E-08 ± 6.7E-09
RB2	0.0506 ± 0.0051	4.82E-08 ± 7.2E-09
RB3	0.0614 ± 0.0074	5.88E-08 ± 4.7E-09
RB4	0.0912 ± 0.0036	1.11E-07 ± 1.2E-08

The results obtained from the water absorption experiment are summarized in Table 3. There was a clear rise in both water absorption coefficient and apparent moisture diffusivity values with increasing bentonite amount in the mix. The water absorption coefficient increased more than 3 times, when bentonite replaced 20% of cement, and up to almost 10

times when the maximum amount of bentonite was incorporated into the mix. The apparent moisture diffusivity increased up to almost twenty times, depending on the amount of used bentonite. Bentonite obviously proved a high absorption capability but its use was accompanied by swelling which resulted in high pressure increase inducing internal stress in the material. The expected sealing effect had thus ambivalent consequences.

Water vapor transport properties were determined using the cup methods. Samples insulated on lateral sides were placed in the cups where a relative humidity environment of 95% and 5% was established using water for wet-cup and silica gel for dry-cup arrangement, respectively. The cups were then placed in a climatic chamber with defined temperature of 20°C and relative humidity of 50%. The difference in partial pressures between the inside and outside environment of the cups induced water vapor diffusion through the samples which was demonstrated by the changes of the samples' weight. After reaching steady state values of mass, the water vapor diffusion resistance factors were calculated [11].

Table 4 shows that also water vapor diffusion properties were significantly affected by the presence of bentonite in the concrete mixtures. The differences were more remarkable for the wet-cup method where the water vapor diffusion resistance factor decreased up to 18 times than for the dry-cup arrangement where an up to four times decrease was observed. It could be explained by the partial transport of capillary condensed water in the wet cup method.

Table 4. Water vapor transport parameters of studied concretes

	Water vapor diffusion resistance factor [-]	
	Dry cup arrangement	Wet cup arrangement
RBR	116.6 ± 14.0	96.7 ± 7.7
RB1	73.7 ± 5.9	15.4 ± 1.8
RB2	70.3 ± 10.5	9.2 ± 0.6
RB3	43.6 ± 1.3	7.7 ± 0.2
RB4	33.2 ± 2.3	5.3 ± 0.4

4 Conclusions

Radioactive waste disposal is indisputably a difficult problem to solve. Deposit sites for this waste must meet many strict requirements to ensure environmental safety. The most important is mitigation of radiation and radionuclide release. Therefore, materials used for this kind of deposits have to serve not only as construction materials, but they also have to guarantee radioactive protection and show superior durability. The aim of this study was to design concrete serving as a barrier to radionuclide transport. For that reason bentonite with great sorption capacity was used as both partial cement replacement and fine filler in the concrete mixture. The experimental results showed that bentonite had no impact on matrix density of concrete but its application led to a high increase of the amount of pores with a diameter of 0.01 to 1 µm. Consequently, the ability of liquid-water and water vapor transport of designed concretes significantly increased but their sorption capacity increased as well which enhanced their capability of radionuclide fixation.

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