PORE STRUCTURE AND TRANSPORT PROPERTIES OF HIGH-VOLUME FLY ASH MATERIALS USED FOR RADIOACTIVE WASTE DISPOSAL FACILITIES

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Abstract
Specifications for underground disposal facilities for radioactive wastes with multi-complex artificial barriers providing different functions are currently studied in Japan. A specific mortar layer with high content of mineral admixtures is expected to prevent diffusion of nuclide molecules emitted from radioactive wastes in groundwater to outer environment. In general, transport properties of porous media depend not only on the total porosity, but also on the pore size distribution, the connectivity of the pore structure, the formation of hydrated compounds, physicochemical reactions and so on. In this study, various measurements on four different mortar mixtures, varying proportion of fly ash to binder with the same high amount of limestone, have been performed at given ages. They consist of compressive strength, porosity accessible to water and to mercury, electrical resistivity, apparent gas permeability and apparent chloride diffusion coefficient. As a result of comprehensive measurements, it has been quantitatively identified that the remarkable evolution of pore structures occurred, but only after a long period of time due to pozzolanic reactions, depending on the fly ash content. Consequently, the transport properties measured on the mortars with high content of fly ash were very low, in spite of high total porosity.

1. INTRODUCTION
The current design concepts for radioactive waste repositories in Japan, comply with performance-based approaches. Among the facility elements constituting the multi-complex artificial barriers with different expected functions, this study focuses on a specific mortar layer, designed to prevent diffusion of nuclide molecules for very long-term. The mixture of this layer contains a high proportion of fly ash, which is expected to reduce hydrate heat generation high-possibly inducing cracks and subsidiarily to lower the pH for prevention of alkali-silica reaction, as well as to change the physical and chemical properties of the hardened material in particular relevant to durability. Transport properties closely linked with
durability depend not only on the total porosity, but greatly also on the geometrical pore system (in particular tortuosity and conductivity), which may be complexed with the progress of hydration and pozzolanic reactions in saturated conditions for a long time. Accordingly, in this study an exhaustive approach will be undertaken on the general properties associated with potential durability of different mortar mixtures with various fly ash contents.

2. MATERIALS

Table 1 shows the four different mortar mixtures used for the tests in this study. While each mixture contains the same high amount of limestone, the mass proportion of fly ash to binder was determined as 0, 10, 20 and 30% respectively. The following materials were used for all the mixtures: OPC (CEM I 52.5 PM ES CP2), fly ash “EDF” used also in French national project “BHP 2000” associated with durability of concrete, limestone “Pikkety”, and sand “Seine” (maximum particle size was smaller than 4mm). The final amount of admixture was determined to satisfy the proper fresh-performance as high fluidity mortar in each case.

Table 1: Mortar mixtures used for the tests in this study

<table>
<thead>
<tr>
<th></th>
<th>W/C (%)</th>
<th>Prop. of FA (%)</th>
<th>W/B (%)</th>
<th>W/P (%)</th>
<th>Air (%)</th>
<th>Ws (kg)</th>
<th>C (kg)</th>
<th>FA (kg)</th>
<th>LS (kg)</th>
<th>S (kg)</th>
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<td>45</td>
<td>0</td>
<td>45</td>
<td>28</td>
<td>60</td>
<td>2.5</td>
<td>230</td>
<td>511</td>
<td>0</td>
<td>307</td>
</tr>
<tr>
<td>FA10</td>
<td>50</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>230</td>
<td>460</td>
<td>51</td>
<td>307</td>
</tr>
<tr>
<td>FA20</td>
<td>56</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>230</td>
<td>409</td>
<td>102</td>
<td>307</td>
</tr>
<tr>
<td>FA30</td>
<td>64</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>230</td>
<td>358</td>
<td>153</td>
<td>307</td>
</tr>
</tbody>
</table>

3. TEST METHODS

Fresh mortar was cast into a cylindrical mould without adding vibration or sticking. All the samples were demoulded 24 hours after casting and then were water-cured at T=20±2°C until the start of preconditioning and testing. A series of measurements relevant to mechanical strength, microstructural characterization and transport properties have been performed at the ages of 90, 120, and 180 days and in the case of compressive strength tests, measurement of porosity accessible to water and mercury intrusion tests, they were performed also at the age of 28 days. In principle, triplicate samples were used in each test as described below.

3.1 Compressive strength test

Characteristic of compressive strength is considered as a basic property parameter to evaluate material quality. This result can be used to study the influence on macro strength, induced by changes in the pore structure due to slow hydraulic and pozzolanic reactions under water curing, in comparison with other tests regarding microstructural characterizations. A sample for this test was a cylinder, the diameter 70 mm and the height 140 mm.

3.2 Electrical resistivity

Since electric current is propagated mainly via saturated pore spaces, the connectivity of the pore structure of a saturated medium is characterized indirectly by measuring electrical resistivity. A sample was the same sized cylinder as in the case of compressive strength test.
and was saturated in water under vacuum before this measurement. The technique used to measure electrical resistivity refers to the literature\textsuperscript{1}.

3.3 Porosity accessible to water

Porosity accessible to water is a prime parameter in evaluation and prediction of durability and a global parameter related to the material quality. This measurement was assessed by hydrostatic weighing, according to the AFPC-AFREM procedure\textsuperscript{2}. The sample was the same one as used for the measurement of electrical resistivity as described above.

3.4 Mercury intrusion test

Mercury intrusion porosimetry, MIP test, is one of the methods widely used for measurement of pore size distribution of porous media. This test enables to characterize pore structures within a wide range. In this study, the measurement has been performed according to LCPC test procedure\textsuperscript{3} and the pressure applied was up to 400MPa. As a pretreatment, the crushed samples were freeze-dried with immersion in liquid nitrogen and were vacuumed for 72 hours before the measurement to remove water in liquid or vapour phase in all the pores.

3.5 Gas permeability test

An apparent gas permeability, which depends on the type of fluid and the applied pressure, is determined by measuring the flow of gas passing through a test specimen in a steady-state condition and applying Darcy’s law. In this study, the permeability tests by using oxygen gas have been performed at a constant pressure gradient, 0.1MPa, according to the recommended method in France\textsuperscript{4} and then the apparent coefficients $K_a$ have been measured on the mixtures, FA0 and FA30. A sample for this test, with thickness (T) 50mm and diameter (D) 110mm, was cut from the central zone of a 110×220mm cylinder. The coefficient was calculated with the average of triplicate tests under the same curing condition as shown in Figure 1.

![Figure 1: Procedure of the gas permeability test](image)

3.6 Apparent chloride diffusion coefficient

In a saturated condition, the chloride diffusion coefficient can be determined by a test of natural diffusion or migration under an electrical field. In this study, two types of chloride penetration tests have been performed in a saturated condition to obtain the apparent chloride diffusion coefficient according to the following procedures.

**Non-steady-state migration test in a saturated condition**

There are various experimental techniques and calculation methods for migration tests under an electrical field. In this study, the migration tests have been performed in a saturated condition, at $T=20±2\,^\circ\text{C}$, according to a method similar to that proposed by Tang & Nilsson\textsuperscript{5,6}. After vacuum saturation with a 0.1M-NaOH solution, each sample ($T=50\text{mm, }D=110\text{mm}$) cut
after 90 or 180day water-curing was mounted between two compartments of a migration cell. The upstream contained 30 g L\(^{-1}\) NaCl + NaOH 0.1M, while the initial downstream solution was NaOH 0.1M. In general, state of chloride ion ingress into a concrete can be experimentally obtained from a chloride concentration profile. Nevertheless, a colorimetric method has been studied as an alternative to assess chloride diffusion coefficient more simply from the chloride penetration depth \(x_d\). Note that the literature\(^7\) revealed a good accordance in the comparison between the apparent chloride diffusion coefficient \(D_{ns}\) assessed from the \(x_d\) measured by a colorimetric method and the application of the modified Nernst-Planck equation proposed by Tang under the assumption of very dilute solutions (see equation (1))\(^5\) and by means of a profile method. Therefore, only the colorimetric procedure by AgNO\(_3\) method has been applied in this study.

\[
D_{\text{ref}(\text{seg})} = \left( \frac{R \cdot T}{Z \cdot F} \right) \left( \frac{e}{\Delta E} \right) \left( \frac{x_j - \alpha \sqrt{x_j}}{t} \right), \quad \alpha = 2 \cdot \left( \frac{R \cdot T}{Z \cdot F} \right) \left( \frac{e}{\Delta E} \right) \cdot \text{erf}^{-1} \left( 1 - 2 \cdot \frac{c_d}{c_s} \right)
\]

(1)

where \(t\) denotes the test duration (s), \(Z\) the valence of chloride ion (\(Z=1\)), \(F\) the Faraday constant (\(F=96480 \text{ J} \cdot \text{V}^{-1} \cdot \text{mol}^{-1}\)), \(e\) the thickness of the specimen (m), \(E\) the actual potential drop between the surfaces of the specimen (V), \(R\) the gas constant (\(R=8.3144 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\)), and \(T\) the absolute temperature (K), and where \(c_s\) and \(c_d\) denote the chloride concentration at the surface of the specimen and at a distance \(x_d\) from the exposure surface, respectively.

**Non-steady-state diffusion test in a saturated condition**

N-s-s diffusion tests have been performed after 90day water-curing. Each sample (height between 85mm and 100mm) was formed by cutting off the top part of a 70×140mm cylinder. The surface of the sample was coated with epoxy resin, except for the freshly sawed surface intended for chloride exposure. After vacuum saturation with a 0.1M-NaOH solution, the samples were partially immersed in a closed container in the solution (30 g L\(^{-1}\) NaCl + NaOH 0.1M) for 90days at \(T=20\pm2\) . To assess the apparent chloride diffusion coefficient \(D_{ns(dif)}\) after the n-s-s diffusion tests, a profile method on a replicate of the same mixture measured by a colorimetric method in advance has been performed in the contrastive case of FA0 and FA30. As regards FA10 and FA20, only colorimetric methods have been applied. After the diffusion tests, the “total” or “free” chloride concentration profiles have been obtained by titration according to the recommended procedure\(^8\), after dry-grinding of the samples and extraction by nitric acid or by distilled water respectively. From the determination of the concentration profiles, it is possible to assess the coefficient \(D_{ns(dif)}\) by fitting the profile calculated by an analytical solution of Fick’s second law (see equation (2)) by means of a non-linear regression analysis using the least square method to the experimental one\(^9\).

\[
c(t, t) - c_i = (c_s - c_i) \cdot \left[ 1 - \exp \left( - \frac{t}{2D_{ns(dif)}} \cdot \frac{x}{x_d} \right) \right]
\]

(2)

Equation (2) can be similarly applied in case of assessment of \(D_{ns(dif)}\) by means of a colorimetric method. However, in this study, neither the surface chloride concentration \(c_s\) nor the “total” or “free” chloride concentration \(c_d\) at the chloride ingress front \(x_d\) was experimentally assessed, except for FA0 and FA30. Therefore, the value of \(c_d/c_s\) was assumed.
to be 0.14 in all the cases, referring to the theoretical value proposed by Tang for n-s-s migration tests under the assumption of condensation phenomenon. In addition, in case of FA0 and FA30, the values of $c_s$ and $c_d$ experimentally obtained by the profile method were also applied to equation (2) with the penetration depth $x_d$ obtained by AgNO$_3$ method to compare both apparent diffusion coefficients assessed by theoretical and experimental values.

4. RESULTS AND DISCUSSIONS

4.1 Mechanical strength and characterization of the pore structure

The results of the MIP tests at the ages of 28 and 180 days are displayed in Figure 2. The pore size distributions of FA20 and FA30 revealed a bimodal one at the age of 28 days, but while the transition from a bimodal to a monomodal mode occurred, the pore mode shifted towards smaller radii with time. Then, an extreme radius peak appeared around 10 nm at the age of 180 days. Such a transition towards a finer pore structure appeared more remarkably with higher content of fly ash in the mixture and it is supposed to be induced by pozzolanic reactions, filling relative large capillary pores with C-S-H after a long time.

Figure 3 exhibits the relation between the porosity accessible to water and to mercury. It reveals that whereas the porosity accessible to mercury decreased steadily with time whatever mixtures, the porosity accessible to water has changed very little, in particular, with high content of fly ash. In other words, this finding corresponds to the significant change of the relative balance of pore volumes in which a part of capillary pores accessible to mercury has been subdivided into very small pores within a few nanometers range accessible only to water.

The results of the compressive strength tests at given ages are displayed in Figure 4. Whereas the strength at the age of 28 days followed the inverse proportion of fly ash content, the differences decreased with time. It is generally known that the strength depends on characteristics of a transition zone around an aggregate and it was reported that a transition zone of ordinary mortar/concrete includes capillary pores from 50 nm to 2000 nm. Therefore, the relation between the strength and the porosity associated with pore radii higher than 50 nm per cement paste by volume was plotted in Figure 5. In this figure, the good correlation observed between both parameters suggests that the strength depends on the capillary pores with radii higher than 50 nm whatever mixtures. Similarly, the results of the electrical resistivity tests and the correlation with the similar range pores are displayed in Figure 4 and Figure 5, respectively. The resistivity at the age of 90 days does not display a large difference among the mixtures, but it increases remarkably with higher content of fly ash, inducing a large difference with time. The correlation between both parameters is not as clear as in the case of the compressive strength (see Figure 5) and it should be noted that the resistivity is higher at similar porosity as the mixture includes a higher fly ash content. This was expected since resistivity mainly depends not only on the total porosity (including very small pores accessible only to water), but also on the pore system tortuosity and the electrical conductivity of the pore solution, which are greatly changed by pozzolanic reactions.
Figure 2: Pore size distributions of the four different mixtures measured by MIP tests at the ages of 28 and 180 days

Figure 3: Relation between the porosities accessible to water and to mercury

Figure 4: Compressive strength (or electrical resistivity) at the ages of 28, 90, 120 and 180 days

Figure 5: Correlation between compressive strength (or electrical resistivity) and MIP porosity associated with pore radii higher than 50 nm

Transport properties relevant to durability

Figure 6 exhibits the variations in the apparent gas permeability $K_a$ as a function of degree of saturation for FA0 and FA30 at the ages of 90 and 180 days. In comparison with the coefficients between different ages on the same mixture, the difference observed with FA30 was larger than that observed with FA0. This derives from the fact that whereas the capillary pores of FA0 with radii higher than 100 nm, which are considered to dominate in the gas permeability process, have not remarkably changed during the period, the pore mode of FA30 has shifted towards smaller radii, reaching the extreme peak around 10 nm (see Figure 2). Such a transition enabled large capillary pores to be filled with C-S-H to interrupt preferential access paths for gas with progress of pozzolanic reactions for a long time. Further, in comparison with the coefficients between both mixtures at the same age, that of FA30 was
smaller than that of FA0 by one order of magnitude. Likewise, it can be deduced that this improvement derives from the characteristics of pore structures complicated by pozzolanic reactions as described above.

The apparent chloride diffusion coefficients $D_{\text{ns(mig)}}$ assessed from the measurement of the average chloride penetration depth $x_d$ by AgNO$_3$ method and application of Tang’s formula (equation (1)) after the n-s-s migration tests on the four different mortar mixtures at the ages of 90 and 180 days are compared in Figure 7. This figure reveals that the value of $D_{\text{ns(mig)}}$ was smaller with higher content of fly ash in the mixture and that it decreased remarkably due to the evolution of pore structures induced by pozzolanic reactions and to the modification of ionic interaction between hydrated compounds. This tendency agrees with the laboratory and field data reported in the literature$^{12,13}$.

Likewise, the results of the apparent chloride diffusion coefficients $D_{\text{ns(dif)}}$ assessed from the ‘total’ and ‘free’ chloride concentration profiles and by a colorimetric method substituting the theoretical $c_d/c_s$ value (=0.14) or the experimental value obtained by the concentration profile, according to Equation (2), after the n-s-s diffusion test for 90 days are summarized in Table 2 (which includes also $D_{\text{ns(mig)}}$ assessed from the n-s-s migration test at the age of 90 days as described above). This table reveals that the coefficient assessed by a colorimetric method substituting the theoretical $c_d/c_s$ value was much smaller than others, but at the same time this discrepancy was greatly improved by substituting the experimental $c_d/c_s$ measured at the chloride exposure surface and at the chloride ingress front. Consequently, such a discrepancy possibly derives from the uncertainty of the theoretical value to the diffusion tests showing a very small chloride penetration depth measured by a colorimetric method, such as the mixtures with high content of fly ash tested in this study. Moreover, in comparison with the coefficient between $D_{\text{ns(mig)}}$ and $D_{\text{ns(dif)}}$, it can be observed that the relation of $D_{\text{ns(mig)}} > D_{\text{ns(dif)}}$ exists in both cases of FA0 and FA30. This finding agrees well with the features reported in the literature$^{7,14}$. 
Table 2: Comparison between the apparent chloride diffusion coefficients $D_{ns(mig)}$ assessed by a colorimetric method after n-s-s migration test, and $D_{ns(diff)}$ assessed by a profile method and by a colorimetric method after n-s-s diffusion test (at the age of 90 days)

<table>
<thead>
<tr>
<th>FA0</th>
<th>$D_{ns(mig)}$ (Color. Method)</th>
<th>$D_{ns(diff)}$ (Profile Method)</th>
<th>(Profile Method)</th>
<th>$D_{ns(diff)}$ (Color. Method)</th>
<th>(Color. Method)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(10^{-12} \text{ m}^2/\text{s})$</td>
<td>$D_{ns(diff)}$</td>
<td>$c_d/c_s=0.14$</td>
<td>$c_d/c_s$ (Exp. ’free’)</td>
<td>$c_d/c_s$ (Exp. ’total’)</td>
</tr>
<tr>
<td>FA0</td>
<td>14.2</td>
<td>6.5</td>
<td>10.5</td>
<td>1.4</td>
<td>8.1</td>
</tr>
<tr>
<td>FA10</td>
<td>11.1</td>
<td>---</td>
<td>---</td>
<td>1.1</td>
<td>---</td>
</tr>
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<td>FA20</td>
<td>7.9</td>
<td>---</td>
<td>---</td>
<td>0.7</td>
<td>---</td>
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<td>5.8</td>
<td>3.2</td>
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<td>0.3</td>
<td>3.1</td>
</tr>
</tbody>
</table>

5. CONCLUSION

A series of measurements relevant to mechanical strength, microstructural characterization and transport properties on the four different mortar mixtures have been performed at given ages in this study. These results yield the following remarks:

- In the case of incorporation of high volume of fly ash in the mixture, the pore size distribution has remarkably changed for a long time with the progress of pozzolanic reactions, resulting in the formation of very fine pore structures.
- The compression strength revealed a good correlation with the porosity associated with pore radii higher than 50nm, whatever mixtures.
- The electrical resistivity mainly depends on the total porosity, the pore system tortuosity, and the electrical conductivity of the pore solution, which are greatly changed by pozzolanic reactions of fly ash.
- The apparent gas permeability of FA30 was smaller than that of FA0 by one order of magnitude due to the complicated paths for gas through a very fine pore structure.
- The value of $D_{ns(mig)}$ assessed by n-s-s migration test was smaller with higher content of fly ash in the mixture and it decreased remarkably, due to the evolution of pore structures and to the modification of ionic interaction between hydrated compounds.

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