

Parametric analyses of diffusion of activated sources in disposal forms

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Abstract

The primary objective of a low-level radioactive waste disposal facility is to isolate low-level radioactive waste from the public and the environment until the radionuclides in the waste have decayed to levels at which the hazard is negligible. Two fundamental concerns must be addressed when attempting to isolate low-level waste in a disposal facility on land. The first concern is isolating the waste from water, or hydrologic isolation. The second is preventing movement of the radionuclides out of the disposal facility, or radionuclide migration. Particularly, we have investigated here the latter scenario. Empirical curves describing the progression of the altered zone are obtained and they are used to define the correspondent altered thickness in the numerical calculations for a cement sample. Subsequent numerical analyses of diffusion of activated sources in waste disposals are considered for cemented containers. The adopted DAMAGE code takes into account a mass conservation equation and the linear momentum balance equation for the multiphase material. The mathematical model is based on the theory developed by Bazant for concretes and geomaterials; the fluid phases are considered as a unique mixture interacting with a solid phase. Short- and long-term diffusion analyses are performed for different characteristics of the grout and the results are presented in terms of radionuclides concentration. Indications on the minimum grout thicknesses able to resist to radioactive fluxes up to 1000 years are given. © 2004 Elsevier B.V. All rights reserved.

Keywords: Radionuclide; Cemented material; Grout; Transport mechanism; Diffusion

1. Introduction

The primary objective of a low-level radioactive waste disposal facility is to isolate low-level radioactive waste from the public and the environment until the radionuclides (radioactive atoms) in the waste have decayed to levels at which the hazard is negligible. The radioactive substances [1] can be generally grouped into two categories: nucleuses resulting from fissions (fission products, among which isotopes ^{90}Sr , ^{137}Cs and ^{85}Kr , with half times up to 30 years, are the most dangerous) and those formed through neutronic absorption in fissile and fertile elements. Nowadays about 2000 different radionuclides are known, characterised by chemical properties, decay mechanisms, types of radiations and ener-

getic spectrum. Obviously, the longer is their average life, the weaker is the specific radioactivity. About 70 radionuclides have average lives longer than some months: just these ones are important for the radioactive disposals. The wastes with high activity contain, in a concentrated form, 95% of the global waste activity. Two fundamental concerns must be addressed when attempting to isolate low-level waste in a disposal facility on land. The first concern is isolating the waste from water, or hydrologic isolation. The second is preventing movement of the radionuclides out of the disposal facility, or radionuclide migration. Our purpose is to consider the latter scenario.

Migration of radionuclides [2] may occur when water comes into contact with low-level radioactive waste and carries the radionuclides into the surrounding soil/structure. The radionuclides are likely to migrate more rapidly when coarse-grained deposits, like sand and gravel, exist in the surrounding

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soil. Keeping water out of trenches reduces radionuclide migration. Disposing of low-level radioactive waste in a liquid form can increase migration of radionuclides away from the disposal facility. Liquid low-level waste has been found to be corrosive and can damage containers in which it is buried. If the liquid waste leaks from its container, it can migrate from the disposal facility.

2. Radionuclides transport in cemented repositories

The transport rate through engineered barriers (compacted bentonite clay and cement) is mainly diffusion controlled, but due to the strong sorption behaviour of the materials, the diffusion rate of the radionuclides is much slower than in pure water. In clay diffusion experiments, a thin clay plate containing the radioactive isotope is usually inserted into the center of a clay plug, and after an appropriate time has elapsed, the plug is sectioned and each slice is measured for radioactivity. From the measurements, the “apparent” diffusivity is calculated which includes the sorption retardation.

The long term stability of cement paste has been studied in [3] with a static leaching technique. Crushed cement paste has been leached with typical saline and non-saline deep granitic groundwater. The data of the analysis of the equilibrated leach water has then been used for computer modelling of the evolution of degrading cement. The results indicate a stability in respect to maintain a $\text{pH} > 12.5$ for some hundred thousand years assuming a diffusion controlled leaching process.

Concrete is likely to be used in considerable quantities in repository construction for high and low level wastes. The hydrated cement will contact water and generate conditions that constitute a long-term chemical barrier to radionuclide migration as a result of decreased solubility and strong adsorption. These conditions maintain a high pH, associated calcium ions in solution and a large surface area of solids with adsorption properties. However, other radionuclides exist (e.g. U, Tc) which behave otherwise [4]; in fact, insoluble U(VI) phases can become soluble in solutions of high pH, low carbonate, and high concentrations of alkaline earth cations [5]. Some industries (e.g. [6]) propose the disposal of low and high level radioactive waste by extensive use of concrete based on Ordinary Portland Cement (OPC) and related products. These materials act as structural components and physical barriers to radionuclide migration in the short term and as a chemical barrier in the long term. The variation of physical and chemical properties of these materials with both time and temperature are important factors in maintaining the structural and barrier properties for the timescale requirements. This is particularly important for the long-term maintenance of chemical barrier performance since this only depends on the presence of materials of desirable chemistry and thus will continue to be effective long after the physical integrity of the waste container or repository is degraded. The chemical barrier properties of the cementitious materials are a consequence of two main factors. The first factor is the dissolution

of the hydrated cement compounds from the water environment surrounding the radioactive waste which generates a high pH (in the region 12) which in turn leads to low solubility for many long lived radio elements (e.g. Am; however, as stated above, this is not true for any radionuclide). The second factor is that the hydrated cement compounds have a very high specific surface area, which provides a good substrate for the adsorption of radionuclides from solution and leads to their immobilization. Estimates of the timescale for maintaining chemical barrier performance, based on the chemistry of hydrated cements, indicate extremely long times, of the order of 10^5 years [7].

The longevity of manufactured materials in the repository environment over such long periods of time is subject to significant uncertainty [8]. At the same time, the prediction of material performance is essential in the development and use of waste packages (waste forms and waste containers). In the absence of a good mechanistic understanding of a material's performance and data that span a wide range of the expected performance and physicochemical conditions, extremely conservative assumptions need to be considered. Many of the performance predictions rely on data collected over a relatively limited range of test conditions; thus, extrapolation of these data requires good mechanistic understanding [7,9]. Without proper data support, any benefits that the waste forms or container might provide could be ignored; hence, it is highly desirable to improve the predictability of the materials performance. This also requires demonstration of quality control of the product.

3. Colloids

Colloid-facilitated radionuclide transport [10] is considered an important mechanism in the models used for predicting radionuclide migration through engineered barrier systems and the surrounding geological formations of repositories for radioactive waste. Colloids may facilitate radionuclide migration from the repository to the biosphere if: (1) colloids are present in sufficient concentrations; (2) radionuclides are bound onto the colloid material and (3) colloids are mobile in subsurface environments. In the near field of a repository, corrosion of container material and the degradation of backfill material may produce colloids. In addition, colloids are abundant in groundwater systems. Due to their relatively high surface area, colloids are effective carriers of contaminants. Moreover, substantial evidence for the generation and existence of colloids in high pH cement-type environments is proved.

Other complete mathematical models describing radionuclides transport (such as the ones by [11,12]) are available in literature but they mainly consider groundwater flows phenomena. Additionally, necessary simplified assumptions are considered in the numerical analyses, hence decay, volatilisation, hydrodynamic dispersion or coprecipitation of radionuclides with secondary solids and dissolution processes

[13,14] etc., are here neglected (or treated with sensible simplifications).

The complexity of the transport mechanism will certainly require further investigations, even if the aim of this study is to give, in the absence of a good mechanistic understanding of a material's performance and data that span a wide range of the expected performance and physical–chemical conditions, conservative assumptions and define a safety scenario.

4. Cemented materials and degradation through contact with radioactive wastes

Ultra-high performance cement-based materials like reactive powder concretes (RPC) have been submitted to a leaching test in [15]. Microscopic observations have shown that de-ionised water leaching altered the matrix microstructure and that the ground quartz, fine sand and steel fibres were not involved in the degradation process.

A leaching test simulates the worst attack of a container confining radioactive waste during its service life of 300–500 years. In this severe test, the sample is immersed in a de-ionised water bath [16]. The water is renewed often and maintained at a pH level as low as 7. Carbonation is avoided by bubbling nitrogen in the deionised water. After 6 months of leaching, a sample extracted from the solution exhibits a superficial degradation clearly observed in a backscattered electron image, i.e. a sound zone underneath an altered porous zone in which anhydrous silicates C_3S and C_2S are dissolved.

An estimation of the degraded zone gives:

$$d_{mm} = 4.52 \times 10^{-2} \sqrt{t} \quad (1)$$

where d_{mm} is the depth of the damaged zone after a given time t .

The mechanism of degradation is the consequence of the diffusion of dissolved species from the material towards the solution. Hence, the RPC matrix is durable as long as a sound zone persists.

Another method is presented by [17] for mortar specimens, which accelerates cement hydrate dissolution by increasing Ca^{2+} ion moving speed in the pore water by applying a constant potential gradient across a mortar specimen in contact with water. With this method, the ions moving are not the same as under natural condition, but similar deterioration conditions are obtained.

The studies presented above, together with those presented by [18], have shown the relevance of the concept of local chemical equilibrium for understanding the degradation of cement pastes. This approximation holds when the kinetics of diffusion are slower than the kinetics of reaction inside the paste. It is particularly well-adapted to the case of the degradation of a Portland cement paste. In this case, a layer of very low solubility forms at the surface of the paste and does not dissolve on observable time scales. The diffusion takes place between a fixed solid–liquid interface and a dif-

fusion front, which moves towards the core of the paste. The diffusion kinetics slow down with time and, after a transitory time, the conditions for local chemical equilibrium are achieved inside the sample. It was shown that the degree of leaching (degraded depth and quantity of the various leached species) is proportional to the square root of time. In addition, abrupt edges of dissolution are by [18] predicted and observed. If surface dissolution can be neglected, degradation is controlled by diffusion and the thickness of the degraded zone (e) obeys a law of the form (compare with Eq. (1)):

$$e = \sqrt{D_{app}t} \quad (2)$$

where D_{app} is the apparent diffusion coefficient.

The speed of progression of the diffusion front is then:

$$V_1 = \frac{de}{dt} = \frac{\sqrt{D_{app}}}{2\sqrt{t}} \quad (3)$$

Hence, two different regimes (diffusion versus surface dissolution) occur during demineralised-solution-induced degradation of cement pastes. The rate of superficial layer dissolution is negligible only if the solubility of the C–S–H in the superficial layer is slow and so the kinetics of degradation is proportional to the square root of time, otherwise the speed of dissolution of the superficial layer is equal to the speed of advancement of the diffusion boundary. However, when cement paste is degraded by natural water (e.g. in equilibrium with granite or clay), or infrequently renewed demineralised water, ions naturally present or leached into the solution will increase the stability of the superficial layer or maintain the rate of dissolution of this layer at a negligible level over a long period of time.

5. The numerical model

5.1. Balance equations

The conservation of the water content w , i.e. the mass of the whole free water (not chemically bound) per m^3 of concrete which can evaporate at a given temperature ($105^\circ C$) may be expressed as [19]

$$\frac{\partial w}{\partial t} = -\text{div } \mathbf{J} + \frac{\partial w_d}{\partial t} \quad (4)$$

where \mathbf{J} is the flux of relative humidity [$kg/m^2 s$] and w_d represents the total mass of free water released in the pores by drying.

The heat balance requires that

$$\rho C \frac{\partial T}{\partial t} - C_a \frac{\partial w}{\partial t} - C_w \mathbf{J} \nabla T = -\text{div } \mathbf{q} \quad (5)$$

where T is the temperature, ρ the mass density of concrete, C the isobaric heat capacity of concrete (per kilogram of concrete) including chemically bound water but excluding free water, C_a the heat of sorption of free water (per kilogram of free water); C_w the isobaric heat capacity of bulk (liquid)

water; $C_w \mathbf{J} \nabla T$ the rate of heat supply due to convection by moving water and \mathbf{q} is the heat flux. Usually, the term of heat convection is negligible, but in rapid heating it might not be so.

The linear momentum balance equation for the whole multiphase medium, neglecting inertial forces, is [20]

$$\operatorname{div} \sigma + \rho^m \mathbf{g} = 0 \quad (6)$$

where σ is the total stress, ρ^m the density of the multiphase medium (concrete plus water species) and \mathbf{g} an acceleration related to gravity.

5.2. Constitutive equations

5.2.1. Heat and moisture flux

The heat flux q is due to temperature gradient (governed by Fourier's law) and to moisture concentration gradient (Dufour's flux)

$$\mathbf{q} = -a_{T_w} \nabla w - a_{T_T} \nabla T \quad (7)$$

where the coefficients a_{T_w} , a_{T_T} depend on w and T .

Due to the negligible contribution of the moisture flux, Eq. (7) is re-written as

$$\mathbf{q} = -a_{T_T} \nabla T \quad (8)$$

The flux of humidity may be written as [21]

$$\mathbf{J} = -c \nabla h \quad (9)$$

where h is relative humidity (ratio between actual vapour pressure p and vapour pressure at saturation p_s) and c is called permeability, function of h and T . The relation between relative humidity and water content at variable temperature is

$$dh = k dw + K dT + dh_s \quad (10)$$

in which $K = (\partial h / \partial T)_w$ is the hydrothermal coefficient representing the change in h due to one-degree change of T at constant w ; dh_s is the self-desiccation and $k = (\partial h / \partial w)_T$ is the cotangent of the slope of the isotherm $w = w(h)$.

5.2.2. Equation of state for pore water

For temperatures $T < 374.15^\circ\text{C}$ (critical point of water) we must distinguish between saturated, $p > p_s(T)$, and partially saturated concrete, $p \leq p_s(T)$ (p being the pressure of both vapour and water, because capillary pressure effects are neglected).

5.2.2.1. *Partially saturated concrete.* From experimental data [22–24] it was seen that the following semi-empirical expression is acceptable

$$\frac{w}{c} = \left(\frac{w_1}{c} h \right)^{1/m(T)} \quad \text{for } h \leq 0.96 \quad (11)$$

in which

$$h = \frac{p}{p_s(T)} \quad m(T) = 1.04 - \frac{T'}{22.34 + T'}$$

$$T' = \left(\frac{T + 10}{T_0 + 10} \right)^2$$

T is expressed in $^\circ\text{C}$; $T_0 = 25^\circ\text{C}$; c is the (dried) cement mass per m^3 of concrete; w_1 is the saturation water content at 25°C .

5.2.2.2. *Saturated concrete.* The thermodynamic properties of water can be taken into account in terms of specific volume of water, v , as a function of T and p , $v = v(T, p)$. In this way, the effect of porosity variation and of volumetric elastic expansion can be described by [25]

$$w = \frac{(1 + 3\varepsilon^V)\phi}{v} \quad \text{for } h = (p/p_s) \geq 1.04 \quad (13)$$

where

$$d\varepsilon^V = \frac{d\sigma^V}{3K} + \alpha dT; \quad \sigma^V = \phi p \quad (14)$$

ϕ : porosity; ε^V : linear volumetric strain of concrete due to the stress in the fluid phase σ^V ; K : expansion modulus; α : coefficient of linear thermal expansion of concrete, typically, $12 \times 10^{-6} \text{C}^{-1}$.

The variation of porosity with temperature (and hence with the variation of water quantity) is here neglected. Other simplifying assumptions will be considered.

Usually concrete is in unsaturated conditions, but if fully saturated regions appears ($h = 100\%$), this situation is covered using values of diffusivity in saturated concrete D_{sat} ranging from 10^{-8} to $10^{-4} \text{m}^2/\text{s}$. Compared to normal diffusivities in non-saturated concrete, these values are several orders of magnitude higher. Possible situations where this effect appears are concrete dams or offshore platforms where a discontinuous jump of diffusivity is to be expected at the interface between saturated and non-saturated concrete. Once fully saturation occurs, and since pore pressure is equivalent to hydraulic height, pore pressure gradient is equivalent to an hydraulic gradient and it is dealt with in the model. For more details see e.g. [26,27].

5.2.3. Concrete permeability

It is assumed that the flux of moisture inside the concrete is controlled by the minimum transverse section of the pores, or "necks", in the flux tubes through the cement paste.

An acceptable form for permeability [21] is

$$\text{for } T \leq 95^\circ\text{C}, \quad a = a_0 f_1(h) f_2(T) \quad (15a)$$

$$\text{for } T > 95^\circ\text{C}, \quad a = a'_0 f_3(T) \quad (15b)$$

with $a'_0 = a_0 f_2(95^\circ\text{C})$; a_0 is the reference permeability at 25°C .

The temperature of 95°C is chosen as the beginning of this transition. The function $f_1(h)$ reflects the moisture transfer in the layers of water adsorbed inside the necks and in agreement

with [21,28]

$$\begin{aligned} f_1(h) &= \bar{\alpha} + \frac{1-\bar{\alpha}}{1+((1-h)/(1-h_c))^4}, & \text{for } h \leq 1 \\ f_1(h) &= 1, & \text{for } h > 1 \end{aligned} \quad (16)$$

where $h_c \cong 0.75$ = humidity of transition; $\bar{\alpha} \cong 1/20$ at 25 °C.

At $T = 95$ °C it is assumed that the necks are sufficiently large to allow the flow of both liquid water and water vapour phases. Hence $\bar{\alpha}$ is equal to 1 at 95 °C. Between 25 and 95 °C a linear interpolation of $\bar{\alpha}$ is assumed. If the curve is extended below 25 °C, the relation $1/\bar{\alpha} = 1 + 19(95 - T)/70$ seems more appropriate.

f_2 in Eq. (15a) is given by an Arrhenius' type equation

$$f_2 = \exp \left[\frac{Q}{R} \left(\frac{1}{T_{0a}} - \frac{1}{T_a} \right) \right]; \quad T \leq 95 \text{ °C} \quad (17)$$

with T_{0a} and T_a absolute temperatures; Q activation energy for the migration along the multimolecular layers of water adsorbed inside the necks; R gas constant.

In accordance with [21], $Q/R \cong 2700$ K and a good choice for $f_3(T)$ is given by

$$f_3(T) = \exp \left(\frac{T - 95}{0.881 + 0.214(T - 95)} \right); \quad T > 95 \text{ °C} \quad (18)$$

in which T is expressed in °C and the numerical constants are taken from interpolation of experimental data.

The permeability is also largely influenced by the hydration degree (or aging). Referring to the available data, this dependence seems to be well described by

$$a_0 = a_1 \times 10^{\sqrt{a_2/t_e}} \quad (19)$$

with t_e : equivalent period of hydration (maturity, see below).

The values of $a_1 = 10^{-13}$ m/s, $a_2 = 40$ days agree with the data by [25].

5.2.4. Hydration and drying of concrete

The hydration degree can be conveniently referred to the period of equivalent hydration, t_e , which represents the period of hydration at 25 °C in water, necessary to confer the same hydration degree which is assumed at the real time t and with the actual history of variable h and T . It is defined, for $0 < T < 100$ °C, as

$$t_e = \int_0^t \beta_T \beta_h dt \quad (20)$$

The coefficient β_T is a function of temperature and, since the chemical reaction of hydration is a process which is thermally activated, it can be expressed, together with β_h , as [28]

$$\beta_T = \exp \left[\frac{U_h}{R} \left(\frac{1}{T_{0a}} - \frac{1}{T_a} \right) \right], \quad \beta_h = [1 + \bar{\alpha}(1 + h)^4]^{-1} \quad (21)$$

where R is the gas constant, U_h the activation energy of hydration, T_a and T_{0a} are absolute temperatures.

From the interpolation of experimental results by [25] at 25 °C, it was found that

$$w_h(t_e) \approx 0.21c \left(\frac{t_e}{\tau_e + t_e} \right)^{1/3}; \quad \tau_e = 23 \text{ days} \quad (22)$$

The amount of dehydrated water, w_d (per m³ of concrete), can be expressed as

$$w_d = w_h^{105} f_d(T) \quad (23)$$

where w_h^{105} represents the hydrated water content at 105 °C and $f_d(T)$ gives the functional dependence of dehydrated water amount on temperature. Typical $f_d(T)$ functions are available in [29], where they are obtained through interpolation of experimental data.

5.2.5. Heat capacity and heat of sorption of concrete

The heat capacity of concrete, ρC , consists of the heat capacity, $\rho_s C_s$, of the solid microstructure, excluding hydration water (per m³ of concrete), less the loss of heat due to drying. Hence [19],

$$\rho C \frac{\partial T}{\partial t} = \rho_s C_s \frac{\partial T}{\partial t} - C_d \frac{\partial w_d}{\partial t} \quad (24)$$

The heat of sorption, C_a , due to the presence of water, can be expressed as the difference between latent heat of water (mainly represented by evaporation heat of liquid water) and the heat of sorption, C_{ad} , of water over the pore walls,

$$C_a \frac{\partial w}{\partial t} = \frac{\partial [w_c H(p, T)]}{\partial t} - C_{ad} \frac{\partial w_{ad}}{\partial t} \quad (25)$$

where H is the enthalpy of liquid water as a function of p and T , given by the thermodynamic tables of vapour; w_c quantity of capillary water (per m³ of concrete); w_{ad} the quantity of adsorbed water; $w = w_c + w_{ad}$ (plus the vapour mass, which is negligible).

For a complete explanation of the model, refer to [30].

6. Modelling of radionuclides transport

In accordance with what previously mentioned, the modelling of the radionuclides transport mechanism have been treated in a simplified way in our model but, in order to test its predictive capabilities, the numerical results have been first compared with available experimental and analytical results taken from literature and briefly cited in the previous pages.

It is assumed that the radionuclide transport follows the flow of water inside the grout pores, through a diffusion process similar to the one defining the flux of humidity governed by the moisture concentration gradient (Dufour's flux, see above).

Isothermal conditions apply.

7. Material data

The physical parameters adopted in all the analyses reported here are depicted in Table 1: the values refer to a leaching test on cement paste with diffusion of Ca^{2+} in deionised water but, from a comparison with the data available in literature, referred to radionuclides and recalled before, they seem to be particularly suitable to define also the diffusive transport of these elements. Particularly, the apparent diffusion coefficients D_{app}^i , $i = 1, 2, 3$ (together with $D_{\text{app, mortar}}$ referring to mortar specimens), have been calculated from the effective diffusion D_e through the expression [31], varying the porosity ϕ , the density ρ and the distribution coefficient K_d

$$D_a(\phi + \rho K_d) = D_e \quad (26)$$

Hence, the range of variation for the transport parameters used here is [32–35]

	From	To
D_e	2.37×10^{-13}	$1.82 \times 10^{-9} \text{ m}^2/\text{s}$
ϕ	0.01	0.9
D_{app}	6.97×10^{-15}	$5.21 \times 10^{-11} \text{ m}^2/\text{s}$
K_d	20×10^{-3} , 40×10^{-3} , $100 \times 10^{-3} \text{ m}^3/\text{kg}$	

which can be considered appropriate to model a grout with a water/cement ratio ≤ 0.5 .

Under these assumptions, the empirical curves defining the progression of the degraded zone in time for a cement paste/mortar sample with variable porosity are reported in Figs. 1 and 2 in accordance with Eqs. (1) and (2). Particularly, Eq. (2) is plotted, assuming the values for D_{app} equal to those named “ D_{app}^1 ” according to Table 1.

The curves indicate that the thickness of the altered zone increase with both time and porosity; however, the measure of the thickness of the degraded zone is not enough to fully understand and describe the radioactive transport mechanics and its development in time and inside the con-

Table 2

Mechanical parameters of the grout for the numerical analyses (from [40])

Elastic modulus	$E = 30.5 \text{ GPa}$
Poisson's coefficient	$\nu = 0.18$
Density	$\rho = 2400 \text{ kg/m}^3$
Coefficient of thermal expansion	$\alpha = 6e^{-06} \text{ }^\circ\text{C}^{-1}$
Medium compressive strength	$f_{\text{cm}} = 37 \text{ MPa}$
Medium tensile strength	$f_{\text{ctm}} = 1.7 \text{ MPa}$

crete sample. In fact, no indications exist on the minimum grout thickness to effectively resist to radioactive aggression: the whole sound zone of a cement paste sample is affected by radionuclides and the only way is to estimate its thickness through appropriate numerical models.

8. Numerical analyses

Necessary simplified assumptions have been considered in the numerical analyses (performed with the fully coupled code DAMAGE described in [30,38,39]), as stated above. The complexity of the transport mechanism will certainly require further investigations, however, the huge range of diffusion parameters adopted (see above) allows for obtaining precautionary results for the diffusion of activated sources in cemented disposals. Different possible scenarios are given and analysed here.

The mechanical characteristics of the grout, together with the previously reported diffusion ones, are shown in Table 2: they are in accordance with those required by CEB-FIP 90, already used in [40].

The adopted mesh can be seen in Fig. 3: a slice of a concrete wall has been considered, with a thickness of 30 cm, meshed through quadrilateral 8-node isoparametric element with different dimensions to avoid numerical oscillations in the region of higher diffusion gradients (close to the edge subjected to radioactive flow). The radionuclides have been considered to flow inside the cement paste thanks to the water filling the pores, neglecting accelerating effects due to possible presence of colloids, as previously explained: this

Table 1

Diffusion coefficients varying porosity and K_d (right) adopted in the analyses

Porosity	D_e (calcium) in cement paste (from Mainguy et al. [36])	D_e mortar	D_{app}^1	D_{app}^2	D_{app}^3	$D_{\text{app, mortar}}$	$K_d \times 1000$ (From Baek and Pitt [37])	Density
0.001	2.37158E–13	1.4E–12	6.97503E–15	2.82E–15	9.88E–16	4.12E–14	20	1700
0.01	2.59375E–13		7.62644E–15	3.09E–15	1.08E–15	4.12E–14	40	2100
0.1	6.35096E–13		1.86245E–14	7.55E–15	2.65E–15	4.11E–14	100	2400
0.2	1.71776E–12		5.02269E–14	2.04E–14	7.15E–15	4.09E–14		
0.3	4.64607E–12		1.35454E–13	5.51E–14	1.93E–14	4.08E–14		
0.4	1.25663E–11		3.653E–13	1.49E–13	5.23E–14	4.07E–14		
0.5	3.39885E–11		9.85173E–13	4.02E–13	1.41E–13	4.06E–14		
0.6	9.19294E–11		2.65692E–12	1.09E–12	3.82E–13	4.05E–14		
0.7	2.48644E–10		7.16553E–12	2.94E–12	1.03E–12	4.03E–14		
0.8	6.72513E–10		1.93251E–11	7.93E–12	2.79E–12	4.02E–14		
0.9	1.81896E–09		5.21192E–11	2.14E–11	7.55E–12	4.01E–14		

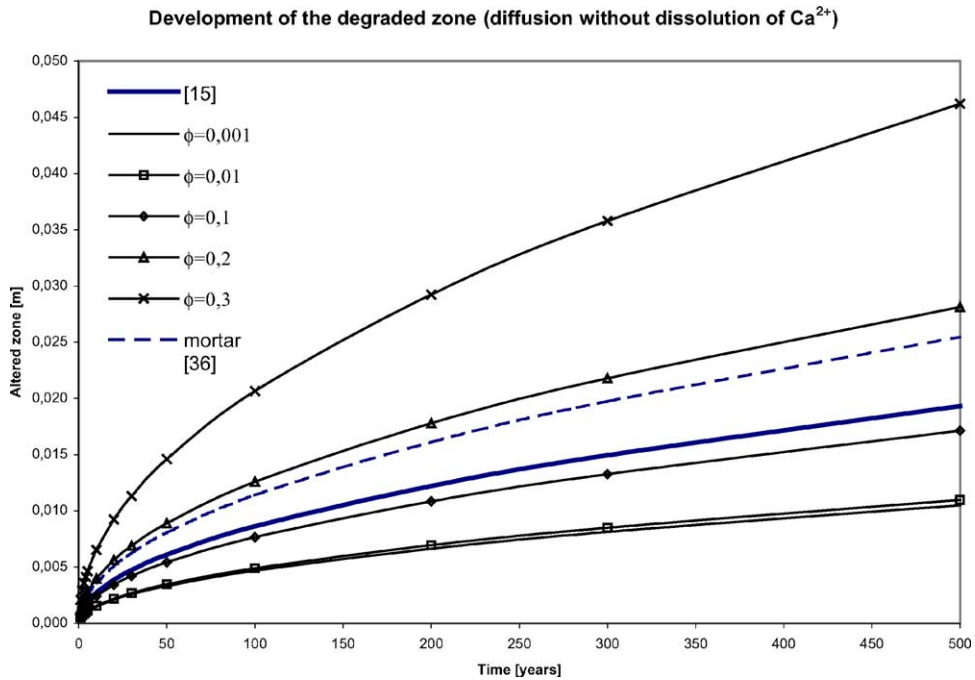


Fig. 1. Empirical curves of diffusion for cement pastes and mortars (from Eq. (2)).

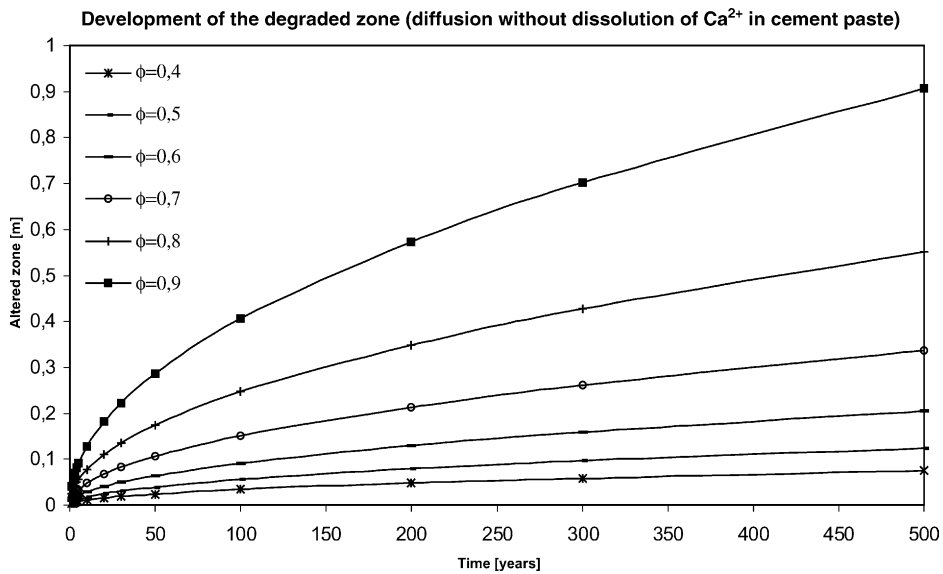


Fig. 2. Empirical curves of diffusion for cement pastes and mortars (from Eq. (2)).

assumption is not restrictive considering the position of the grout in relation to the ground. In fact, the grout is not in contact with groundwater systems (in which the presence of colloids is abundant) and additionally corrosion of contain-

ers material or degradation of backfill material (which may produce colloids) are not expected, at least up to now.

The front of maximum radionuclides concentration, assumed to correspond to $C \geq 88\%$ and indicating the

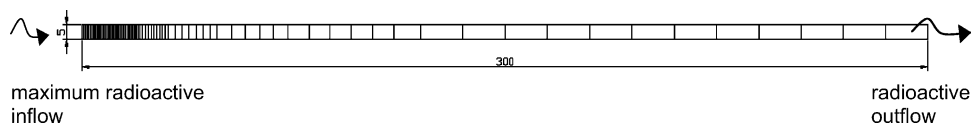


Fig. 3. Mesh adopted in the numerical analyses.

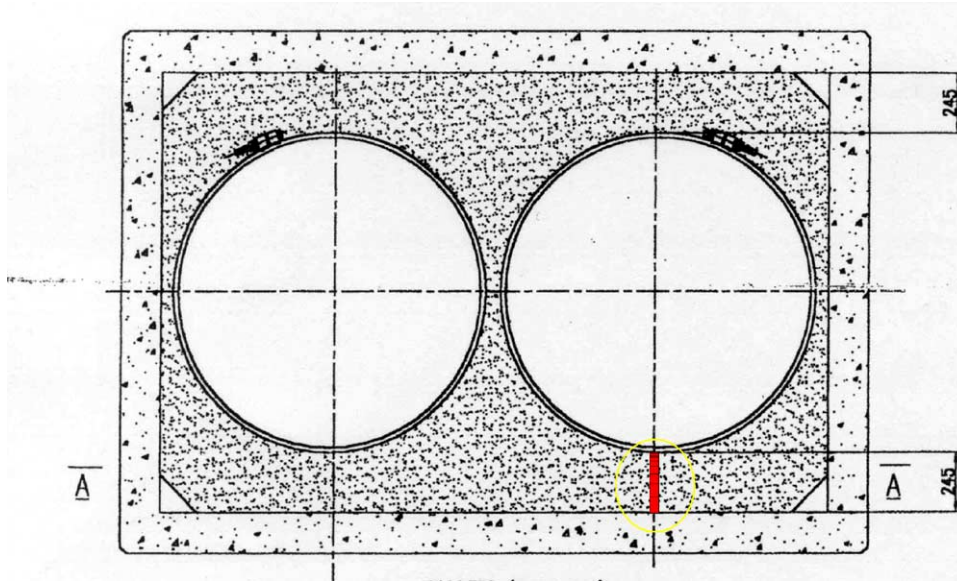


Fig. 4. Position of the studied area related to the storage module.

progression of the altered zone, proceeds in time towards the inner part of the sample; the border of null concentration correspondingly moves with time.

A qualitative position of the meshed area in relation with the storage module, in agreement with the design drawings by ENEA, is indicated in Fig. 4: the radioactive flow is supposed to proceed outwards from the inner containers through the grout.

Regarding the material data diffusivity, permeability and porosity of the grout, reference values in agreement with [40], as already mentioned, have been used; however, they have been appropriately changed to take into account different scenarios of radioactive diffusion in the cement paste.

Particularly, together with the parameters listed in Table 1, the main datum has been shown to be the porosity.

8.1. “Early-years” parametric analyses

First analyses have been performed up to about 50 years varying the porosity of the mixture from 0.12 to 0.7: correspondingly, the input apparent diffusion coefficients vary between 1.86×10^{-14} and 7.17×10^{-12} (see Table 1); these allowed for determining the already mentioned altered zone, sound zone and unaltered core.

The results have been collected in terms of radionuclides concentration in percentage (referred to the maximum

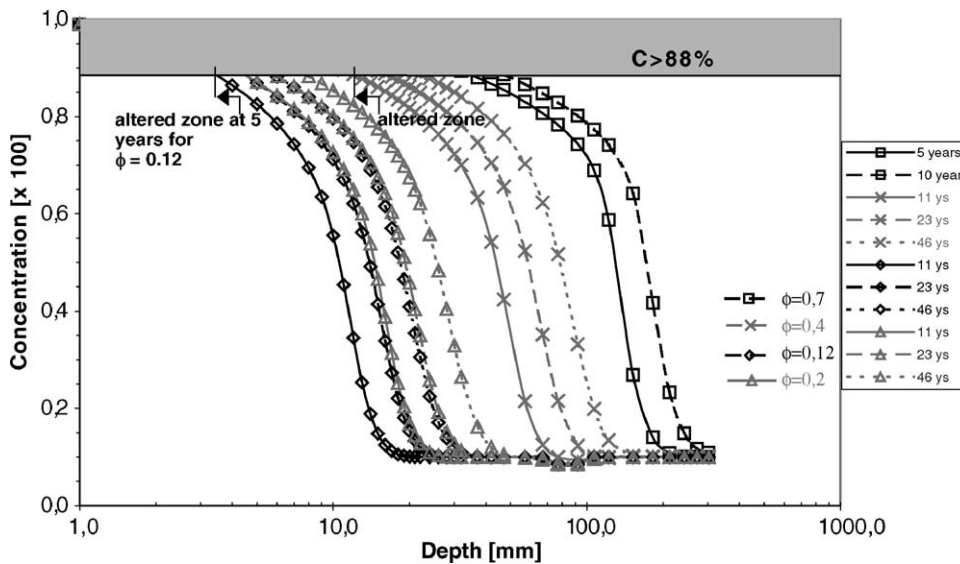


Fig. 5. Radionuclides transport varying porosities — early-years analyses. Percent concentration vs. distance.

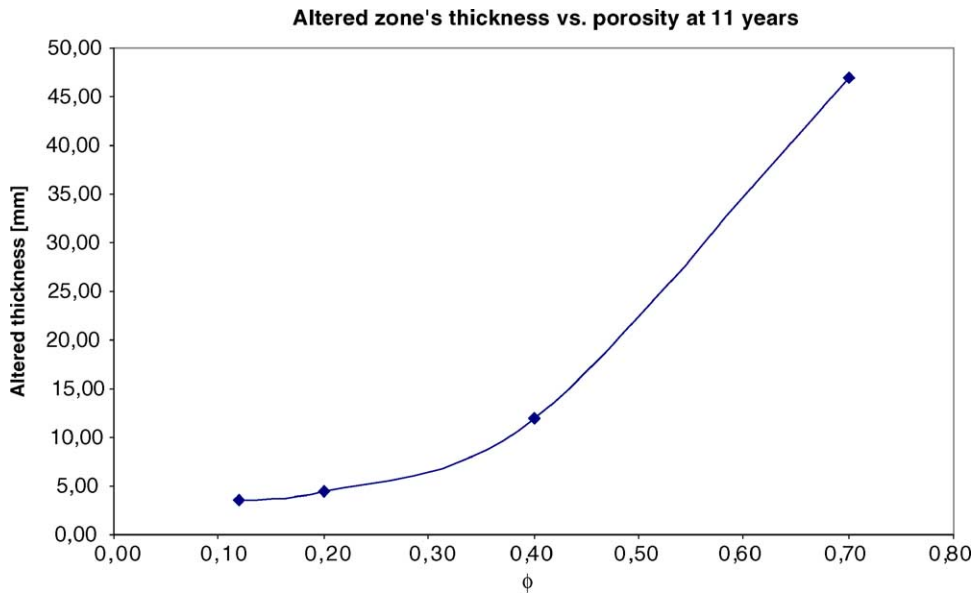


Fig. 6. Relationship between thickness of the altered zone and porosity ($t = 11$ years; numerical results from the early-years analyses).

radionuclides concentration at the inflow border) versus distance, in agreement with available data from literature [11]: the shape of the curves is the same and a comparison with empirical data, as previously exposed, allowed for defining the areas affected by different radionuclides concentrations.

Fig. 5 clearly shows what stated through a semi-logarithmic diagram: an increase in porosity of 3.5 times determines a correspondent increase in the altered zone (zone affected by a concentration of radionuclides higher than 88%) of 7.8 times: the highly non-linear relation between thickness of the altered zone and porosity is shown in Fig. 6 at $t = 11$

years: the altered thickness has been collected from Fig. 5 for a typical time; similar curves could be plotted for further times indicating the same non-linear trend.

The sound zone is clearly defined by the variation of radionuclide concentration once proceeding towards the inner part of the sample.

These first analyses allowed for defining realistic porosities to be used to forecast the transport phenomenon up to 1080 years; acceptable values can be considered to be 0.12, 0.2 and (superior limit) 0.4, obtainable mainly varying the water/cement ratio.

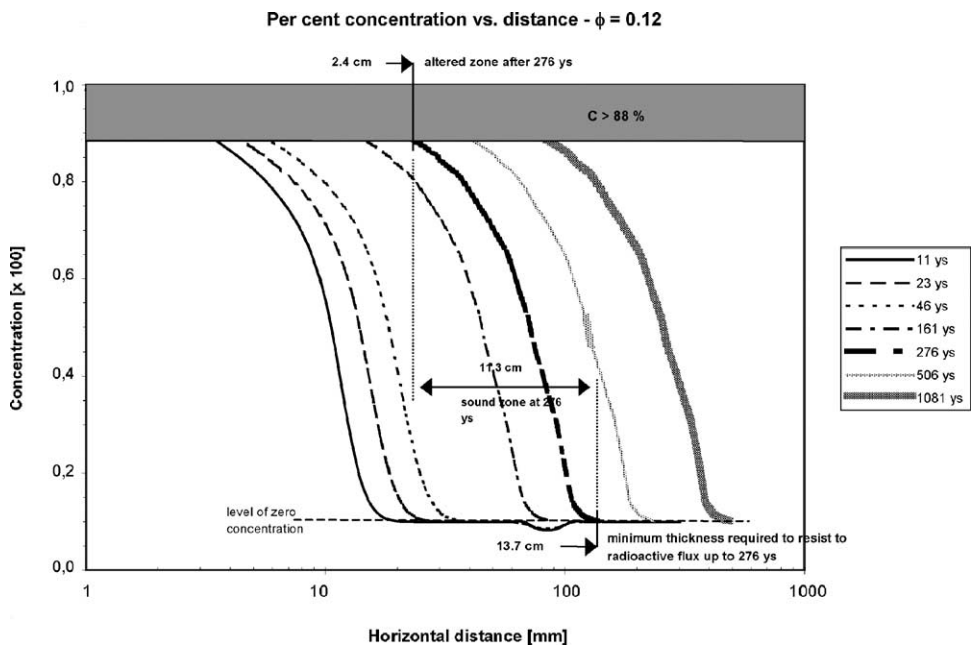


Fig. 7. Radionuclides transport for $\phi = 0.12$.

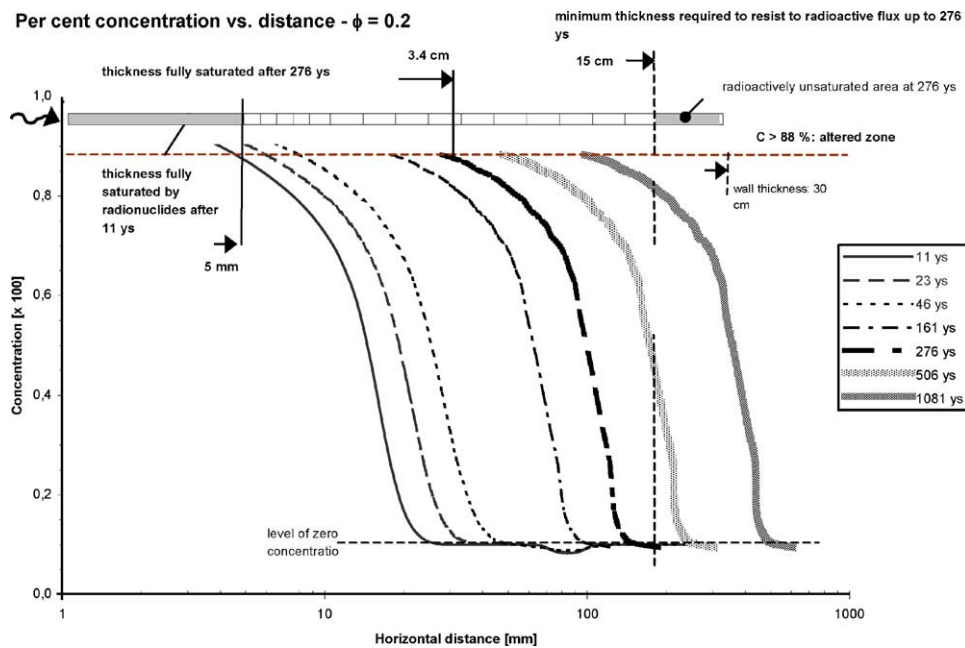


Fig. 8. Radionuclides transport for $\phi = 0.2$ (mesh not in scale).

It is to be added that, for times higher than 500 years, the results have been obtained through extrapolations.

8.2. Numerical predictions up to 1000 years

The analyses have then been pushed forward till reaching 1080 years and the results of radionuclides transport collected for the abovementioned three sets of porosities. The transport parameters and the mechanical data are those used for the early-years numerical analyses listed before.

The curves of radionuclides concentration versus depth of the sample are depicted in Figs. 7–9 and the main results are listed in Table 3.

Hence, the container can be considered safe to radionuclides flow if the grout thicknesses are higher than 13.7, 15 and 38 cm, respectively correspondent to porosities of the mixture equal to 0.12, 0.2 and 0.4.

Table 3

Summary of numerical results (long-term analyses)

Porosity	Altered zone at 300 years (mm)	Sound zone at 300 years (mm)	Minimum thickness of the grout to resist to radionuclides flow up to 300 years (mm)
0.12	24	113	137
0.2	34	116	150
0.4	92	288	380

9. Conclusions

Analytical curves of progression of the degraded zone for a cement sample subjected to a leaching test with demineralised water have been obtained from collection of empirical data taken from literature. The results show the development of the altered zone with time but do not give information on the effective presence of radionuclides beyond the altered zone and on the thickness of the sound zone. However, the mechanism is mainly governed by porosity and the depth of the altered zone is given by Table 4, at $t = 300$ years.

Additionally, numerical long-term analyses of diffusion without dissolution of Ca^{2+} have been performed through a fully coupled numerical code able to reproduce the flow of radionuclides inside a grout sample; the mixture has been chosen in accordance with [40], as previously stated. It has been proved that the transport mechanism is the same as that of radioactive nuclides with low activity. The corresponding results are listed in Table 3 and give indications on the minimum grout thicknesses able to resist to radioactive fluxes up to 300 years. For longer periods, it can be supposed that, as a consequence of decay, the radionuclides activity has reduced to safety levels (however, additional results have been reported

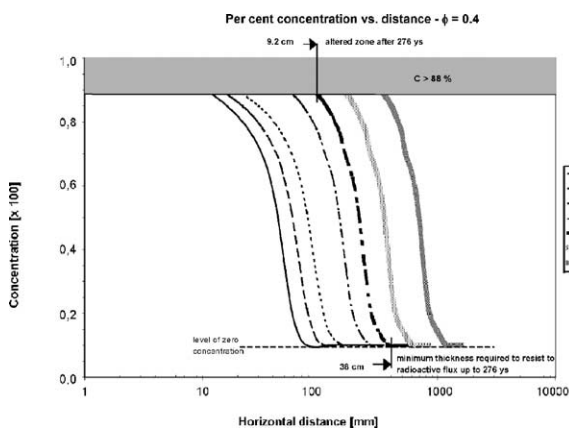


Fig. 9. Radionuclides transport for $\phi = 0.4$.

Table 4
Summary of analytical results at $t = 300$ years (from Eq. (2) and Table 1)

Porosity	Altered zone (mm)
0.1	13.3
0.2	21.8
0.4	58.8

to resist to radioactive fluxes up to 1080 years). A comparison between Tables 3 and 4 shows that (with the same porosity) the numerically predicted altered zone is thicker than the one given by the empirical curves: this can be mainly explained by the fact that, with a simplifying assumption, an area saturated by a minimum of 88% of radionuclides concentration has been considered “altered”.

As a conclusion, a grout sample with porosity variable between 0.1 and 0.2 can be considered to represent an effective safety barrier to radionuclides flux up to 300 years once its thickness is equal or larger than 13.7/15 cm.

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