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Modelling of bituminized radioactive waste leaching. Part I: Constitutive equations

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Abstract

This paper presents theoretical work aiming at studying the behaviour of leached bituminized waste materials and the development of a saline solution-filled pore structure (called permeable layer) in the material. In Part I of this paper, the constitutive model COLONBO which describes mathematically the evolution of the pore structure, the water uptake, the salt and RN release of leached bituminized waste is presented. By the introduction of adequate simplifications, an analytical solution of the problem is obtained which gives the main relations between measurable leaching indicators (water uptake, soluble salt release, porosity profiles and apparent thickness of the permeable layer) and material (soluble salt content, bituminized waste density) or environmental parameters (chemical activity of water in the leachant). In the companion paper (Part II), the validity of these relations is investigated experimentally.

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1. Introduction

Since the late sixties, bitumen has been widely used by the nuclear industry as a matrix for the immobilization of low- and intermediate level radioactive waste originating mainly from the reprocessing of spent nuclear fuel: precipitation or evaporator concentrates, ion exchange resins, incinerator ashes, and filter materials. In France, Bituminized Waste Products (BWP) constitute a non-negligible part, in terms of volume, of the total waste to be disposed of in a (hypothetic) geological repository. As a matter of safety, the long-term performance assessment of the disposals relies therefore on the behaviour of the BWP when brought in contact with groundwater. Research performed at the Atomic Energy Commission since the beginning of the 1990s have therefore focused on the long-term behaviour of bituminized waste, aiming at understanding and

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modelling the consequences of ground-water immersion on the transport properties and radionuclides leaching of bituminized materials [1–3].

In consequence of the chemical process used to solidify liquid concentrates, BWP contain generally some soluble salts ($NaNO_3$, Na_2SO_4) in more or less important quantities, and insoluble elements (precipitation sludge particles, radionuclides, etc). As pointed out in previous investigations, water uptake by bituminized materials can be important and lead to the development of a solution-filled pore structure in which radionuclides and dissolved salts can then migrate [4]. The release of radionuclides and sodium nitrate from BW has been the focus point of many past studies [4–6], mainly because of their potential consequences on clay engineering barriers: released radionuclides represent the source term that will migrate in the barrier, sodium nitrate concentrated solutions can lead to the development of osmotic pressures in clay materials. On the contrary, the origin of BW's leachability, that is to say, the development of a solution-filled pore structure, has been scarcely studied, both on a theoretical point of view and experimentally. To the authors knowledge, only the mathematical models developed at the pore scale by Brodersen [7] have focused on that point.

This paper presents original theoretical work aiming at studying and quantifying the pore structure evolution at the origin of salt and radionuclides leaching in BWP. In Part I of this paper, the mathematical modelling of BW leaching at the macroscopic scale is described, leading a system of non-linear diffusion equations. By the use of adequate assumptions, it is shown that this system can be solved to obtain analytical expressions which relate measurable leaching indicators (water uptake, soluble salt release, thickness of the permeable layer) to BW's and leachant's key-parameters (soluble salt content, effective diffusion coefficients of water and salts, chemical activity of water). In the companion paper (Part II), numerous ESEM observations performed on different BW materials leached by more or less aggressive solutions are used to demonstrate the validity of these analytical relations.

2. Phenomenology and state equations

2.1. Phenomenology

The behaviour of leached BWP depends on the physical properties of bitumen, on the chemical composition of the embedded waste, and on the chemical environment at the repository. The phenomena taking place in leached BWP are still a matter of discussion in the scientific community. Nevertheless, based on the available studies on the subject and on the work performed at the Atomic Energy Commission since the early 1990s on 'soft' bitumen,[1] the following mechanisms have been identified:

- Although bitumen is generally considered as an impermeable material, it has been shown experimentally [1] that water can diffuse in pure bitumen according to a Fickian regime [8,9]. Recent through-diffusion experiments have led effective diffusion coefficients of about $5 \times 10^{-15}\ \mathrm{m^2/s}$ [8,9]. The driving force of water diffusion in pure bitumen is the gradient of chemical potential between the leached surface of the bitumen specimen (in contact with the leachant) and the bulk of the material.
- As soon as the chemical activity of water exceeds that of a saturated solution of the most soluble salts (0.74 for $NaNO_3$) contained in the BWP, the salt grains are dissolved, leading to the creation of pores filled with a saline solution [1,4,7,10]. Scanning Electron Microscopy (SEM) performed on cross sections of synthetic BW samples leached by water shows the presence of bitumen cavities containing water and partly dissolved salt grains, see Fig. 1.
- Once the dissolution of the soluble salt particles has taken place, the 'pumping' of water by the salts leads to the formation of a permeable layer, constituted of pores filled with a saline solution. In consequence of the important volume increase related to the ingress of water, leached BWP swell [4,11]. The Environmental SEM (ESEM) observation of Fig. 2 shows the typical aspect of the permeable layer in a synthetic BW leached by water.
- The outward diffusion of dissolved salts and radionuclides from leached BWP is made possible by the formation of the permeable layer. Recent experiments have shown that the diffusion of sodium and cesium radioactive tracers in pure bitumen layers is not possible or extremely slow

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[1] In France, BWP are cast at moderately high temperatures (120–130 °C) with a soft and fluid bitumen, the Viatotal 70/100 with a penetration depth between 7 and 10 mm and a softening point of 45–51 °C.

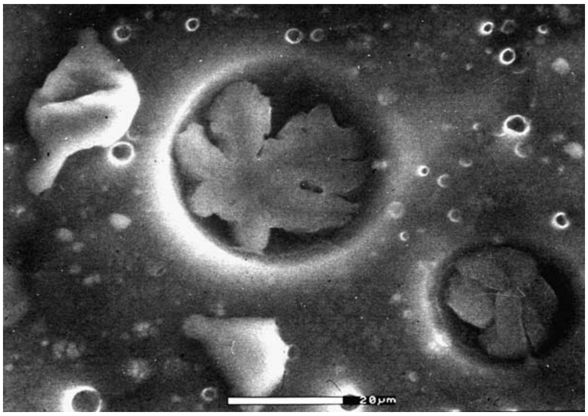

Fig. 1. SEM observation of a synthetic BW leached by water showing the presence of bitumen cavities filled with partially dissolved salt.

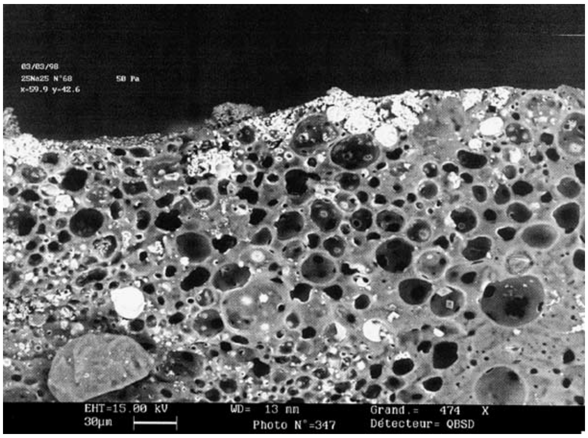

Fig. 2. ESEM observation of a leached synthetic BW showing the typical aspect of the permeable layer (bubbles filled with a saline solution).

[8,9]. This means that some modifications of the bitumen films surrounding the solution-filled cavities must take place to permit the release of dissolved salts and RN [4,12]. Two main hypotheses have been proposed in the past to explain this phenomenon:

- Local swelling due to the formation of pores filled with saline water leads to a high stretching of the bitumen film surrounding the cavities, making them permeable to dissolved salts.
- Excessive local swelling leads to an interconnection of the cavities and therefore to the formation of a connected porosity in the BWP [4].

Diffusion of water in the permeable layer (1–3×10^{-13} m^2/s) occurs at a much greater rate than in pure bitumen (5×10^{-15} m^2/s), according to recent through-diffusion experiments performed on completely leached BW samples [8,9] (i.e., completely leached means that the membranes are in equilibrium with the leachant). Pore interconnections are also assumed to be at the origin of these results.

2.2. Mathematical model

2.2.1. Basic assumptions

The following assumptions have been introduced to build a mathematical model describing the leaching behaviour of BW:

- The scale of description considered in the proposed mathematical model is macroscopic, i.e., no distinction is made between salt grains, solution filled pores and the bitumen matrix. BW is therefore treated as an homogeneous medium. This approach differs in that sense from the work of Brodersen [4,7], where diffusion processes were studied at the pore scale.
- The chemical composition of the waste immobilized in the bitumen matrix can vary significantly. In order to simplify the system, the model is based on a reference BW, constituted of a ‘soft’ bitumen matrix embedding a single soluble salt, sodium nitrate ($NaNO_3$). In a first approximation, the behaviour of other solubles salts, such as Na_2SO_4, is assumed to be similar to that of sodium nitrate.
- The chemical behaviour of sodium nitrate ($NaNO_3$) is supposed to be unaffected by the embedding process.
- The volume occupied by insoluble salts is associated to the volume occupied by pure bitumen. Accordingly, the waste is assumed to be composed of two phases: bitumen and insoluble salts on the one hand, dissolved sodium nitrate and water (which constitute the solution filling the pores of leached BW) on the other hand. For a standard waste, this assumption leads to a 10 % overestimation of the bitumen volume fraction.
- The condition of ‘local equilibrium’ is assumed to be valid in all the bituminized material, i.e., the chemical activities of water in the bitumen matrix and in the saline solution filling the pores are equal at any time.

- Dissolved salts, radionuclides and water migrate in leached BW according to the first of Fick's diffusion laws.
- Leached BW is considered as an open porous medium. Boundary conditions (salt and water concentrations) are therefore given by the external medium, i.e., the leachant. This choice is motivated by the careful analysis of through-diffusion experiments which demonstrate that only pore connectivity can explain the observed increase of diffusion coefficients when comparing bitumen to leached BW [8,9].
- The swelling of the waste is supposed to proceed without any mechanical constraint (i.e., the volume of expansion is not limited).

2.2.2. Schematic representation

According to the phenomenology and the assumptions above-mentioned, leached BW can be described in a 1D Cartesian coordinate system as constituted of two different layers (see Fig. 3):

- The unleached layer (no. 1): in this area, water diffuses in the bitumen matrix without dissolving the soluble salts (assimilated to sodium nitrate). The chemical activity of water remains strictly inferior to that of water in a sodium nitrate ($NaNO_3$) saturated solution (i.e., $a_w < a_d$ with $a_d \approx 0.74$ for a $NaNO_3$ saturated solution). No increase of volume is observed in this layer.
- The permeable layer (no. 2): in this area, the activity of water a_w exceeds a_d ($a_d \approx 0.74$ for a $NaNO_3$ saturated solution) and reaches that of the leachant (a_o) at the BW/leachant interface. In the permeable layer, the soluble salts (assimilated to sodium nitrate) are dissolved, leading to the formation of pores filled with a more or less concentrated saline solution. Water, dissolved salts and radionuclides diffuse in this layer with different rates, according to their transport properties.

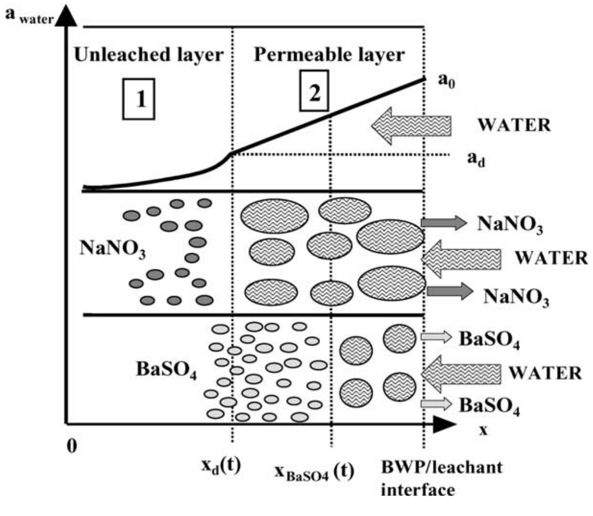

Fig. 3. Schematic representation of leaching mechanisms in bituminized waste.

The two layers are separated by the soluble salts dissolution front (coordinate: $x_d(t)$), which corresponds to the position at which the chemical activity of water a_w reaches the value a_d ($a_d \approx 0.74$ for a $NaNO_3$ saturated solution). The progression of the soluble salts dissolution front towards the center of the BW specimen (coordinate $x = 0$) is controlled by the diffusion rates of water and dissolved salts in the permeable layer.

Concerning the release of radionuclides, due to the diversity of the radioelements embedded in BWP, and due to the lack of detailed information on the speciation of these compounds in the waste form, a global approach has been adopted. Accordingly, insoluble salts ($BaSO_4$, CoS, etc.) and radionuclides are treated in a similar manner: if a sufficient quantity of water is present, the dissolution of these species takes place followed by their migration out of the leached BW. A distinct solubility is attributed to each compound, which leads to the formation of a specific dissolution front for each element (e.g. $x_{dBaSO_4}(t)$ for $BaSO_4$, see Fig. 3). However, the progression of these dissolution fronts is always limited by the position of the soluble salts dissolution front, i.e., $x_d(t)$, which also characterizes the progression of the permeable layer.

2.2.3. Constitutive equations

First of all, the bitumen wasteform is assumed to be composed of two phases: bitumen and insoluble elements on the one hand, pores filled with dissolved salts and water (solution-filled pores) on the other hand. In consequence, the sum of the volume fractions of the two phases is equal to unity

$$p_b(x,t) + p_s(x,t) = 1 \tag{1}$$

with p_b and p_s, respectively as the volume fraction of bitumen (+ insoluble elements) and of solution filled pores in the BW (m^3/m^3). Note that $p_s = p_s(x,t)$ and

$p_b = p_b(x, t)$ vary in time and space, due to the swelling of the BW.

Since no pressure is applied to leached BWP, and the temperature is assumed to remain constant, the chemical potential gradients of the different species (water, salts, radionuclides) reduce to the chemical activity gradients. In general, the chemical activity of a species i is related as follows to its molar concentration c_i:

$$c_i = \frac{a_i}{\gamma_i^* V_M} = \frac{a_i}{\gamma_i} \tag{2}$$

with V_M as the molar volume of the solution and γ_i^* the activity coefficient of the species i, which might depend on the chemical activity a_i. To simplify the constitutive equations listed below for a 1D Cartesian coordinate system, $\gamma_i = \gamma_i^* V_M$ will be referred to as the activity coefficient of the species i.

In the unleached layer (layer no. 1, see Fig. 3), bitumen is the main existing phase. As shown by experimental results, water can diffuse in pure bitumen. Controversy holds concerning the state of water in bitumen, whether it is solubilized in the matrix or contained in some micro-pores. Whatever its state, the transport of water in bitumen can be characterized by two parameters: $D_{w,b}^{eff}$, the effective diffusion coefficient of water in bitumen (m^2/s) and ϕ_b the solubility of water in bitumen or the (micro-) porosity of bitumen (m^3/m^3). According to Fick's first and second laws, the molar balance equation of water in the unleached layer is given by

$$\frac{\partial}{\partial t}\left(\frac{\phi_b p_b}{\gamma_w} a_w\right) = \frac{\partial}{\partial x}\left(\frac{D_{w,1}^{eff}}{\gamma_w}\frac{\partial a_w}{\partial x}\right) \tag{3}$$

with a_w and γ_w respectively as the chemical activity of water and the activity coefficient of water in the solution filling the micro-pores of bitumen. $D_{w,1}^{eff}$ is the effective diffusion coefficient of water in the unleached layer. Note that in the unleached layer, the bitumen volume fraction p_b is close to unity (the soluble salts being not dissolved, the volume fraction of solution-filled pores is negligible). In a first approximation, the effective diffusion coefficient of water in the unleached layer can therefore be taken equal to that of water in pure bitumen, $D_{w,1}^{eff} \approx D_{w,b}^{eff}$.

In the permeable layer (layer no. 2, see Fig. 3), the two phases, i.e., bitumen and solution-filled pores, co-exist. In consequence, the molar balance equation of water takes the following form:

$$\frac{\partial}{\partial t}\left[\left(\frac{\phi_b p_b + p_s}{\gamma_w}\right) a_w\right] = \frac{\partial}{\partial x}\left(\frac{D_{w,2}^{eff}}{\gamma_w}\frac{\partial a_w}{\partial x}\right) \tag{4}$$

with $D_{w,2}^{eff}$ the effective diffusion coefficient of water in the permeable layer (m^2/s). Note that $(\phi_b p_b + p_s)$ represents the total porosity available to water in the permeable layer, part of it related to the bitumen phase (micro-porosity or solubility ϕ_b), most of it associated to the solution-filled bubbles (p_s). Note that according to the hypothesis of a 'local equilibrium', the activity of water in bitumen equals that of water in the solution-filled pores.

The frontier between the unleached and the permeable layers depends on the position of the soluble salts dissolution front. Its progression is related to the quantity of water available at this interface to dissolve the salts, i.e., to the difference between the water fluxes in the permeable and the unleached layers. The dissolution of salts is assumed to be instantaneous. The molar quantity of water needed to dissolve all the soluble salts (assimilated to sodium nitrate) contained per unit volume of BW (mol/m^3) is noted q. The molar balance equation of water at this interface is therefore given by

$$-\frac{D_{w,2}^{eff}}{\gamma_w}\left(\frac{\partial a_w}{\partial x}\right)_{x_d(t)^+} + \frac{D_{w,1}^{eff}}{\gamma_w}\left(\frac{\partial a_w}{\partial x}\right)_{x_d(t)^-} = q\frac{dx_d(t)}{dt} \tag{5}$$

with $x_d(t)$ as the position of the soluble salts dissolution front (m). Eq. (5) implies that the progression of the permeable layer in leached BW depends mainly on the diffusion of water.

The diffusion of soluble salts is assumed to take place only in the permeable layer. The following expression has been adopted concerning the molar balance equation of salts in this layer

$$\frac{\partial}{\partial x}\left(\frac{D_{s,2}^{eff}}{\gamma_s}\frac{\partial a_s}{\partial x}\right) = \frac{\partial}{\partial t}\left(\frac{p_s}{\gamma_s} a_s\right) \tag{6}$$

with a_s as the chemical activity of dissolved salts in the solution-filled pores of the permeable layer, γ_s the activity coefficient of dissolved salts, $D_{s,2}^{eff}$ the effective diffusion coefficient of soluble salts in the permeable layer. Note that only p_s, the volume fraction of solution-filled pores in the BW, is considered for the diffusion of soluble salts.

To close the system of Eqs. (3)–(6), it is necessary to relate the chemical activities of water and dissolved salts in the solution-filled pores of the permeable layer. To this end, the solution is assumed to be composed of dissolved salts and water only, the mixture of the two components being effective without any change of volume. This assumption leads to the following equation:

$$\frac{M_\mathrm{w}}{\rho_\mathrm{w}}\frac{a_\mathrm{w}}{\gamma_\mathrm{w}}+\frac{M_\mathrm{s}}{\rho_\mathrm{s}}\frac{a_\mathrm{s}}{\gamma_\mathrm{s}}=1 \tag{7}$$

with M_s, ρ_s and M_w, ρ_w respectively as the molar (kg/mol) and mass densities (kg/m^3) of sodium nitrate ($NaNO_3$) and water. Note that Eq. (7) is consistent with the definition of standard states for both water and dissolved salts. In the typical case of a solution at infinite dilution (i.e., pure water), $a_\mathrm{s}=0$, $a_\mathrm{w}=1$ and $\gamma_\mathrm{w}=\rho_\mathrm{w}/M_\mathrm{w}=V_\mathrm{M}$, with V_M the molar volume of pure water. Since $\gamma_\mathrm{w}=\gamma^*_\mathrm{w}V_\mathrm{M}$, according to Eq. (2), one recovers the standard definition of the solvent activity coefficient at infinite dilution, i.e., $\gamma^*_\mathrm{w}=1$.

Finally, the release of insoluble elements (mainly $BaSO_4$) and radionuclides can be accounted for by the introduction of two equations. The first one defines the position of the dissolution front for a species i ($i = BaSO_4$, CoS, radionuclides, etc.) and is written as follows:

$$\frac{D^\mathrm{eff}_{i,2}}{\gamma_i}\left(\frac{\partial a_i}{\partial x}\right)_{x_i(t)^+}=\chi_i\frac{\mathrm{d}x_i(t)}{\mathrm{d}t}, \tag{8}$$

where a_i is the chemical activity of species i, γ_i its activity coefficient, $D^\mathrm{eff}_{i,2}$ the effective diffusion coefficient of species i in the permeable layer (m^2/s), χ_i the initial concentration of species i in the BW (mol/m^3) and $x_i(t)$ the position of the dissolution front for species i in the leached BW (m).

The second equation defines the molar balance of a species i in the permeable layer (layer no. 2, see Fig. 3) as follows:

$$\frac{\partial}{\partial x}\left(\frac{D^\mathrm{eff}_{i,2}}{\gamma_i}\frac{\partial a_i}{\partial z}\right)=\frac{\partial}{\partial t}\left(\frac{p_\mathrm{s}}{\gamma_i}a_i\right). \tag{9}$$

Again, note that only p_s, the volume fraction of solution-filled pores in the BW, is considered for the diffusion of a species i.

2.2.4. Numerical implementation

The complex system of constitutive Eqs. (1)–(9) is solved numerically without the need for further simplifications [13]. A finite volume scheme has been adopted for the spatial discretization, ensuring therefore the mass conservation of the system at any time. Owing to swelling of the BW during the calculations, the overall dimensions of the waste product vary in time. To account for this effect, a coordinate change is made to switch from the actual ('swelled') configuration (referenced by the x coordinate) to the initial configuration (referenced by the z coordinate), the latter being fixed in time. At any time, the relation between the z and x coordinates reads as follows:

$$z=x(1-\epsilon) \tag{10}$$

with $\epsilon(x,t)$ as the swelling of the BW. Since swelling occurs only in the permeable layer, it is given by

$$\epsilon(x,t)=\frac{p_\mathrm{s}(x,t)-\dfrac{f_\mathrm{s}\rho_\mathrm{bw}}{\rho_\mathrm{s}}}{1-\dfrac{f_\mathrm{s}\rho_\mathrm{bw}}{\rho_\mathrm{s}}} \tag{11}$$

with f_s the initial soluble salt content of the BW (kg/kg) and ρ_bw its mass density (kg/m^3).

The numerical tool, called COLONBO v2.6 has been developed in Fortran 77 and runs on Microsoft Windows operating system.

3. Parameter study

3.1. Simplified system of equations

The complex system of Eqs. (1)–(11) can only be solved numerically. The meaning and the relative importance of each material parameters (soluble salt content, diffusion coefficients, etc.) and environmental properties (activity of water in the leachant) is not straightforward. To ease the understanding of how salt, radionuclides and water interact in leached BW, further simplifications can be considered, based on experimental observations:

- Diffusion of water in the unleached layer is negligible compared to that of water in the permeable layer, e.g., $D^\mathrm{eff}_{\mathrm{w},1}\ll D^\mathrm{eff}_{\mathrm{w},2}$. Through diffusion experiments performed on completely leached BW samples [8,9] have shown that the diffusion coefficient of water in the permeable layer ($D^\mathrm{eff}_{\mathrm{w},2}=1$–$5\times10^{-13}$ m^2/s) is about a 100 times greater than that of water in pure bitumen ($D^\mathrm{eff}_{\mathrm{w,b}}=5\times10^{-15}$ m^2/s). Accordingly, Eq. (3) for water in the unleached layer might be forgotten. Eq. (5) defining the position of the soluble salts dissolution front can furthermore be simplified as follows:

$$-\frac{D^\mathrm{eff}_{\mathrm{w},2}}{\gamma_\mathrm{w}}\left(\frac{\partial a_\mathrm{w}}{\partial x}\right)_{x_\mathrm{d}(t)^+}=q\frac{\mathrm{d}x_\mathrm{d}(t)}{\mathrm{d}t}. \tag{12}$$

- The pore volume associated to the bitumen phase in the permeable layer ($\phi_b p_b$) can be neglected, compared to that of the solution-filled bubbles (p_s). Solubility of water in pure bitumen (ϕ_b) does in fact not exceed 5% [1,8,9]. In consequence, Eq. (4) for water in the permeable layer might be written as

$$\frac{\partial}{\partial t}\left[\left(\frac{p_s}{\gamma_w}\right)a_w\right]=\frac{\partial}{\partial x}\left(\frac{D^{\text{eff}}_{w,2}}{\gamma_w}\frac{\partial a_w}{\partial x}\right). \tag{13}$$

- The diffusion rate of soluble salts in the permeable layer is small compared to that of water. It has been shown experimentally that the diffusion coefficient of a sodium tracer ($D^{\text{eff}}_{s,2} \leqslant 5\times10^{-15}$ m^2/s) in completely leached BW samples was about 1/100 of that of water ($D^{\text{eff}}_{w,2}\approx 5\times10^{-13}$). Accordingly, at any time, the quantity of soluble salts released from leached BW can be neglected with respect to the initial soluble salt content of the BW. In consequence, the volume fraction of saline solution-filled pores in the permeable layer p_s can be written as follows:

$$p_s = p = \frac{f_s\rho_{bw}\chi_s}{1+f_s\rho_{bw}\chi_s}, \tag{14}$$

where f_s is the initial mass content of soluble salts in the BW material (kg/kg) and ρ_{bw} the mass density of the BW (kg/m^3). Since the micro-porosity ϕ_b of the bitumen phase has been neglected, the volume fraction p_s represents the porosity p of the permeable layer. To avoid confusion, the variable p will be used in the next paragraphs. χ_s in Eq. (14) is the water/soluble salts content ratio of the solution filling the pores (m^3 water/kg soluble salts). One of the main assumptions introduced to establish the COLONBO model is that the chemical behaviour of sodium nitrate ($NaNO_3$), to which all the other solubles salts of the BW are assimilated, remains unaffected by the embedding process. As a result, the water/soluble salts content ratio χ_s reduces to a water/$NaNO_3$ content ratio and can be determined from experimental data on $NaNO_3$ solutions [14], see Appendix A for a complete description of the determination. Since the water/$NaNO_3$ content ratio depends only on the $NaNO_3$ concentration of the solutions, it can be directly related to the chemical activity of water in the $NaNO_3$ solutions, i.e., $\chi_s = \chi_s(a_w)$. Fig. 4 gives a graphical illustration of the $\chi_s(a_w)$ (see Appendix A) and $p = p(a_w)$ relations (see Eq. (14)) for a typical BW with a $NaNO_3$ mass content f_s of 10% and a mass density ρ_{bw} of 1400 kg/m^3.

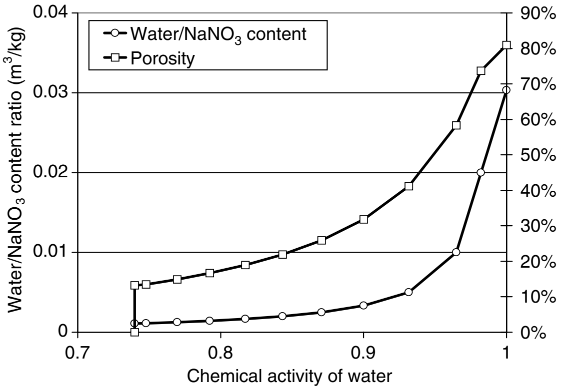

Fig. 4. Water/$NaNO_3$ content ratio and porosity p in function of the chemical activity of water (f_s = 10%, ρ_{bw} = 1400 kg/m^3).

As schematically represented in Fig. 3, the chemical activity of water in the permeable layer of a BW material leached by pure water varies between a_d at the soluble salt dissolution front ($a_d \approx 0.74$ for a $NaNO_3$ saturated solution) and a_o at the BW/leachant interface ($a_o = 1$ for pure water). The evolution of porosity represented in Fig. 4 gives therefore a theoretical representation of the porosity profile that can be expected in the permeable layer of a BW material leached by pure water. The increase of porosity observed near the leached surface of the BW material (where the chemical activity of water equals 1) is to be associated with the important dilution that is necessary to reach chemical activities of water close to 1 in the saline solution-filled pores. Note also the abrupt increase of porosity that takes place near the $NaNO_3$ dissolution front (where the chemical activity of water is approximately 0.74).

- The initial volume content of soluble salts $f_s\rho_{bw}/\rho_s$ of the BW is small when compared to the volume fraction of saline solution p_s. This is true for most of the BWP with f_s typically in the range 0–20% and $\rho_{bw}/\rho_s \approx 0.5$. Hence, Eq. (11) for the swelling of leached BWP can be written as follows:

$$\epsilon \approx p_s \approx p(a_w) \tag{15}$$

and becomes a function of the sole chemical activity of water a_w.

3.2. Analytical solution

Eqs. (12)–(15) form a closed system describing the diffusion of water and the dissolution of $NaNO_3$

in a BW where the consequences of the outward diffusion of dissolved salts on the water molar balance have been neglected. Introducing the change of variable given by Eq. (10), the system can be written with respect to the initial configuration coordinate z in the following form:

$$\frac{\partial}{\partial t}\left[\frac{p(a_{\mathrm{w}})}{1-\epsilon(a_{\mathrm{w}})}\,\frac{a_{\mathrm{w}}}{\gamma_{\mathrm{w}}}\right] = \frac{\partial}{\partial z}\left(\frac{1-\epsilon(a_{\mathrm{w}})}{\gamma_{\mathrm{w}}}D^{\mathrm{eff}}_{\mathrm{w},2}\frac{\partial a_{\mathrm{w}}}{\partial z}\right) \qquad (16)$$

$$-\frac{1-\epsilon(a_{\mathrm{w}})}{\gamma_{\mathrm{w}}}D^{\mathrm{eff}}_{\mathrm{w},2}\left(\frac{\partial a_{\mathrm{w}}}{\partial z}\right)_{z_{\mathrm{d}}(t)^{+}} = \frac{q}{1-\epsilon(a_{\mathrm{w}})}\,\frac{\mathrm{d}z_{\mathrm{d}}(t)}{\mathrm{d}t} \qquad (17)$$

with z_{d} as the position of the $NaNO_3$ dissolution front in the initial configuration (unswelled BW).

Typical leaching experiments consist of 1D tests on samples of initial thickness L with one face in contact with aqueous solutions of variable chemical activity a_{o}. To facilitate the resolution procedure, the local coordinate $Z = L - z$ can be used in Eqs. (16) and (17) instead of z without introducing any changes. As illustrated in Fig. 5, the boundary conditions with the local coordinate Z are given by: $a_{\mathrm{w}}(Z = 0) = a_{\mathrm{o}}$ (the activity of water at the leached surface of the BW equals that of the leachant), $a_{\mathrm{w}}(Z = Z_{\mathrm{d}}) = a_{\mathrm{d}}$ (the activity of water at the $NaNO_3$ dissolution front equals that of a saturated solution of $NaNO_3$, e.g., $a_{\mathrm{d}} = 0.74$). Note that $Z = 0$ now refers to the position of the leached surface of the BW sample.

Eqs. (16) and (17) can be solved analytically if the following simplifications are made:

- The sample can be considered as semi-infinite (the thickness of the permeable layer never exceeds that of the BW sample, i.e., $Z_{\mathrm{d}} \ll L$).
- The porosity p of the permeable layer is constant in time and space. Considering the porosity profile of Fig. 4, this is obviously not realistic. However, by integration of the $p = p(a_{\mathrm{w}})$ profile, one can determine a mean porosity p^m which satisfies the water mass balance in the permeable layer and depends solely on the activity of water in the leachant, i.e., $p^m = p^m(a_{\mathrm{o}})$ [15].

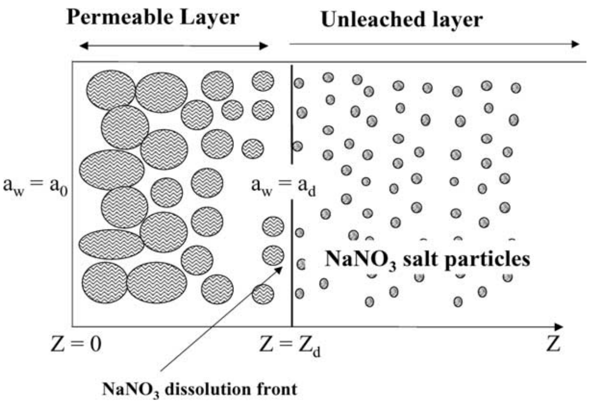

Fig. 5. Schematic representation of leached BW with the Z coordinate system.

$$p^m = \frac{1}{(a_{\mathrm{o}} - a_{\mathrm{d}})}\int_{a_{\mathrm{d}}}^{a_{\mathrm{o}}} p(a_{\mathrm{w}})\,\mathrm{d}a = \frac{f_{\mathrm{s}}\rho_{\mathrm{bw}}\chi^m_{\mathrm{s}}}{1 + f_{\mathrm{s}}\rho_{\mathrm{bw}}\chi^m_{\mathrm{s}}}. \qquad (18)$$

To the mean porosity $p^m(a_{\mathrm{o}})$ corresponds a mean $NaNO_3$/water content ratio $\chi^m_{\mathrm{s}}(a_{\mathrm{o}})$. Fig. 6 represents the evolution of p^m and χ^m_{s} in function of the chemical activity of water in the leachant a_{o} for a standard BW with a $NaNO_3$ mass content f_{s} of 10% and a mass density ρ_{bw} of 1400 kg/m^3.

Similarly, the mole quantity of water per unit volume of BW associated to the progression of the dissolution front can be written as

$$q = \frac{p^m}{\gamma_{\mathrm{w}}}. \qquad (19)$$

Note also that, according to Eq. (15), $\epsilon = p^m$.

The solution of Eqs. (16) and (17) where p has been replaced by p^m is similar to that of general problems of diffusion with an immobilizing chemical reaction [16]. The chemical activity of water is given at any point in the permeable layer by

$$a_{\mathrm{w}}(Z) = a_{\mathrm{o}} + (a_{\mathrm{d}} - a_{\mathrm{o}})\frac{\mathrm{erf}(\eta)}{\mathrm{erf}(\eta_{\mathrm{d}})} \qquad (20)$$

with η given by

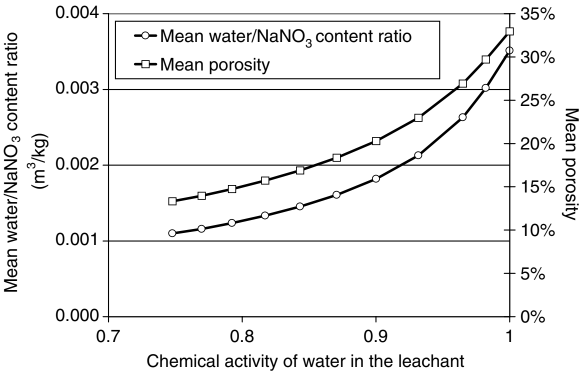

Fig. 6. Mean water/$NaNO_3$ content ratio χ^m_{s} and porosity p^m in function of the chemical activity of water in the leachant a_{o} ($f_{\mathrm{s}} = 10\%$, $\rho_{\mathrm{bw}} = 1400$ kg/m^3).

$$\eta = \frac{Z}{2(1-\epsilon)\sqrt{D^{\mathrm{app}}_{\mathrm{w},2} t}} \tag{21}$$

and erf the error function

$$\mathrm{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y \exp(-p^2)\,\mathrm{d}p. \tag{22}$$

In Eqs. (20) and (21), $D^{\mathrm{app}}_{\mathrm{w},2} = D^{\mathrm{eff}}_{\mathrm{w},2}/p^m$ represents the apparent diffusion coefficient of water in the permeable layer. η_{d} is given by Eq. (21) in which Z is replaced by Z_{d}. By considering time and space conditions such that $\eta \ll 1$, the error function can be approximated as $\mathrm{erf}(y) = 2y/\sqrt{\pi}$. Using this simplification in Eq. (20), the chemical activity of water at any point in the permeable layer reads

$$a_{\mathrm{w}}(Z) = a_{\mathrm{o}} + (a_{\mathrm{d}} - a_{\mathrm{o}})\frac{Z}{Z_{\mathrm{d}}}. \tag{23}$$

From Eq. (23), the chemical activity gradient $\partial a_{\mathrm{w}}/\partial Z = (a_{\mathrm{d}} - a_{\mathrm{o}})/Z_{\mathrm{d}}$ can be estimated. Introduced in Eq. (17), the following expression is obtained for the thickness of the permeable layer in the initial configuration Z_{d}

$$Z_{\mathrm{d}}(t) = \sqrt{\frac{2(1-\epsilon)^2 D^{\mathrm{eff}}_{\mathrm{w},2}(a_{\mathrm{o}} - a_{\mathrm{d}})}{\gamma_{\mathrm{w}} q}}\sqrt{t}. \tag{24}$$

Standard measures during leaching tests include the total water uptake of the specimen $Q_{\mathrm{w}}(t)$, the quantity of leached $NaNO_3$, $Q_{\mathrm{s}}(t)$ and that of other salts and radionuclides for active specimen. These measures are usually expressed as mass or volumes per unit of leached surface area, averaging therefore the behaviour of leached samples. A more intrinsic parameter consist of the thickness of the permeable layer in the initial configuration, Z_{d}. It characterizes the extent of leaching in the specimen, disregarding swelling. However, on a practical point of view, only the apparent thickness of the permeable layer X_{d} (which includes swelling) can be measured experimentally. Using expression (24) for Z_{d} with the change of variable given by Eq. (10) yields X_{d} in the following form:

$$X_{\mathrm{d}}(t) = \sqrt{\frac{2D^{\mathrm{eff}}_{\mathrm{w},2}(a_{\mathrm{o}} - a_{\mathrm{d}})}{\gamma_{\mathrm{w}} q}}\sqrt{t}. \tag{25}$$

According to expression (25), the apparent thickness of the permeable layer evolves proportionally to the square root of time, $\sqrt{t}$. It increases with the chemical activity gradient of water $\sqrt{a_{\mathrm{o}} - a_{\mathrm{d}}}$ and the diffusion coefficient of water in the permeable layer, $\sqrt{D^{\mathrm{eff}}_{\mathrm{w},2}}$. This means that leaching of BW samples by a sodium nitrate saturated solution, i.e., in which $a_{\mathrm{o}} = a_{\mathrm{d}}$, should not lead to the development of a permeable layer. Replacing q in Eq. (25) by its expression in function of p^m yields X_{d} in the following form :

$$X_{\mathrm{d}}(t) = \sqrt{\frac{2D^{\mathrm{eff}}_{\mathrm{w},2}(a_{\mathrm{o}} - a_{\mathrm{d}})}{p^m_{\mathrm{s}}}}\sqrt{t} = \sqrt{\frac{2D^{\mathrm{eff}}_{\mathrm{w},2}(a_{\mathrm{o}} - a_{\mathrm{d}})(1 + f_{\mathrm{s}}\rho_{\mathrm{bw}}\chi^m_{\mathrm{s}})}{f_{\mathrm{s}}\rho_{\mathrm{bw}}\chi^m_{\mathrm{s}}}}\sqrt{t}. \tag{26}$$

According to Eq. (26), the apparent thickness of the permeable layer decreases with increasing soluble salt contents f_{s}. It is in fact inversely proportional to $\sqrt{f_{\mathrm{s}}}$ if swelling is small ($f_{\mathrm{s}}\rho_{\mathrm{bw}}\chi^m_{\mathrm{s}} \ll 1$). This tendency is due to the increasing water supply that is needed to the progression of the soluble salt dissolution front if the soluble salt content f_{s} increases. It means that the higher the soluble salt content of a BW, the slower the leaching kinetics.

A more standard measure on leached BW samples is the water uptake, expressed per unit surface of leached material. In the present analytical resolution, the water uptake $Q_{\mathrm{w}}(t)$ (in kg/m^2) can be easily estimated from the thickness of the permeable layer in the unswelled configuration Z_{d}

$$Q_{\mathrm{w}}(t) = \rho_{\mathrm{w}}(f_{\mathrm{s}}\rho_{\mathrm{bw}}\chi^m_{\mathrm{s}})Z_{\mathrm{d}} = \rho_{\mathrm{w}}\sqrt{\frac{2D^{\mathrm{eff}}_{\mathrm{w},2}(a_{\mathrm{o}} - a_{\mathrm{d}})f_{\mathrm{s}}\rho_{\mathrm{bw}}\chi^m_{\mathrm{s}}}{1 + f_{\mathrm{s}}\rho_{\mathrm{bw}}\chi^m_{\mathrm{s}}}}\sqrt{t}. \tag{27}$$

Expression (27) shows that the water uptake evolves proportionally to the square root of time $\sqrt{t}$, as the apparent thickness of the permeable layer X_{d}. It increases with the gradient of chemical activity of water $\sqrt{a_{\mathrm{o}} - a_{\mathrm{d}}}$ and the coefficient of diffusion of water in the permeable layer $\sqrt{D^{\mathrm{eff}}_{\mathrm{w},2}}$. Theoretically, if swelling remains limited ($f_{\mathrm{s}}\rho_{\mathrm{bw}}\chi^m_{\mathrm{s}} \ll 1$), water uptake increases with the soluble salt content $\sqrt{f_{\mathrm{s}}}$.

Eqs. (26) and (27) have been obtained under the assumption that salt release from leached BW had little impact on the water mass balance in the permeable layer. It does not imply that salt migration is impossible. In consequence, Eqs. (7) and (23) can be used to estimate the salt activity gradient in the permeable layer.

$$\frac{\partial a_{\mathrm{s}}/\gamma_{\mathrm{s}}}{\partial Z} = -\frac{\rho_{\mathrm{s}}}{M_{\mathrm{s}}}\frac{M_{\mathrm{w}}}{\rho_{\mathrm{w}}}\frac{\partial a_{\mathrm{w}}/\gamma_{\mathrm{w}}}{\partial Z} = -\frac{\rho_{\mathrm{s}}}{M_{\mathrm{s}}}\frac{M_{\mathrm{w}}}{\rho_{\mathrm{w}}}\frac{(a_{\mathrm{d}} - a_{\mathrm{o}})}{\gamma_{\mathrm{w}} Z_{\mathrm{d}}}. \tag{28}$$

Table 1
Evolution of the thickness of the permeable layer, of the water uptake, of the soluble salt release, of the porosity with time, with the soluble salt content and with the chemical activity of water in the leachant

	Time, t	Soluble salt content, f_s	Chemical activity, a_o
Apparent thickness X_d	$\sqrt{t}$	$\sqrt{\frac{1+f_s\rho_{bw}\chi_s^m}{f_s\rho_{bw}\chi_s^m}}$	$\sqrt{a_o - a_d}$
Water uptake Q_w	$\sqrt{t}$	$\sqrt{\frac{f_s\rho_{bw}\chi_s^m}{1+f_s\rho_{bw}\chi_s^m}}$	$\sqrt{a_o - a_d}$
Soluble salt release Q_s	$\sqrt{t}$	$\sqrt{\frac{f_s\rho_{bw}\chi_s^m}{1+f_s\rho_{bw}\chi_s^m}}$	$\sqrt{a_o - a_d}$
Porosity	/	$\frac{f_s\rho_{bw}\chi_s^m}{1+f_s\rho_{bw}\chi_s^m}$	Increases with a_o

The quantity of leached soluble salts (assimilated to sodium nitrate) per unit surface of BW is then given by integration of Fick's first law

$$Q_s(t) = -\rho_s \frac{M_w}{\rho_w}(1-\epsilon)D_{s,2}^{\text{eff}} \int_{t=0}^{t} \frac{(a_d - a_o)}{\gamma_w Z_d}\,\mathrm{d}p. \qquad (29)$$

Replacing the thickness of the permeable layer $Z_d(t)$ by its expression (24), and integrating with respect to time leads the salt release in the following form:

$$Q_s(t) = -\rho_s D_{s,2}^{\text{eff}} \sqrt{\frac{2(a_o - a_d)f_s\rho_{bw}\chi_s^m}{D_{w,2}^{\text{eff}}(1+f_s\rho_{bw}\chi_s^m)}}\sqrt{t}. \qquad (30)$$

In Eq. (30), γ_w has been replaced by M_w/ρ_w, i.e., the activity coefficient of water in pure water, as defined by Eq. (2). As shown by Table 2 in Appendix A, considering the activity coefficient of water constant seems a reasonable assumption since it varies little with the $NaNO_3$ content of the pore solution. Note that the quantity of leached soluble salts as given by Eq. (30) shows also a square root of time dependency and increases with the water activity gradient $\sqrt{a_o - a_d}$, the diffusion coefficient of salts in the permeable layer $D_{s,2}^{\text{eff}}$ and the soluble salt content $\sqrt{f_s}$ when swelling is limited ($f_s\rho_{bw}\chi_s^m \ll 1$). On the contrary, it is inversely proportional to the diffusion coefficient of water in the permeable layer $\sqrt{D_{w,2}^{\text{eff}}}$.

Dividing expression (30) for the quantity of leached soluble salts by expression (27) for the water uptake leads the following relation:

$$\frac{Q_s(t)}{Q_w(t)} = \frac{D_{s,2}^{\text{eff}}}{D_{w,2}^{\text{eff}}}\frac{\rho_s}{\rho_w}, \qquad (31)$$

which depends only on the water diffusion to salt diffusion coefficients ratio and on the water to salt mass densities ratio.

Table 1 summarizes the impact of material and environmental parameters on the overall behaviour and pore structure of leached BW, as obtained from relations (14), (26), (27) and (30).

The relations given in Table 1 have been applied to bituminized waste materials containing between 1% and 16% soluble salts and found in good agreement with the numerical results and trends obtained with the COLONBO model [15], as will be shown in Part II of this paper.

4. Conclusions

In this paper, the behaviour of leached bituminized waste materials and the development of a saline solution-filled pore structure has been studied on a theoretical point of view. The constitutive model COLONBO aiming at describing the pore structure, the water uptake, the salt and RN release of leached BW has been presented. BW is considered as an homogeneous material at the scale of mathematical description used in the model, i.e., macroscopic. The equations describe the dissolution of soluble salts contained in the BW, the formation of a permeable layer consisting of solution-filled pores, the resulting swelling of the BW, the diffusion of water, soluble, insoluble salts and RN in this layer. By the introduction of adequate simplifications, an analytical solution for the complex system of coupled diffusion–dissolution–swelling equations has been obtained which gives a good overview of the relations between measurable leaching indicators (water uptake, soluble salt release, porosity profiles and apparent thickness of the permeable layer) and material (soluble salt content) and environmental (chemical activity of water in the leachant) parameters. The companion paper (Part II) presents experimental results which validate qualitatively and quantitatively the trends obtained with the COLONBO model and the proposed analytical solution.

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Appendix A

Ref. [14] gives the evolution of the partial vapor pressure p imposed by $NaNO_3$ solutions at 25 °C in function of the $NaNO_3$ concentrations C of the solutions (g $NaNO_3$/100 g water). The chemical activity of water a_w in the $NaNO_3$ solutions is equal to the following ratio:

$$a_w = \frac{p}{p_o} \tag{32}$$

with p_o as the partial vapor pressure imposed by pure water at 25 °C (3160 Pa). The water/$NaNO_3$ content of the $NaNO_3$ solutions is simply the inverse of the $NaNO_3$ concentrations, i.e., $\chi_s = 1/C$.

Experimental data are summarized in Table 2.

Table 2
Partial vapor pressure p, water/$NaNO_3$ content ratio χ_s, chemical activity a_w and activity coefficient of water γ_w in function of the $NaNO_3$ concentration C of $NaNO_3$ solutions

C (g/100 g water)	p (Pa)	a_w	χ_s (m^3/kg)	γ_w (m^3/mol)
0	3160	1	0.03[a]	0.0180
5	3104	0.982	0.02	0.0182
10	3050	0.965	0.01	0.0184
20	2945	0.932	0.005	0.0188
30	2845	0.9	0.0033	0.0191
40	2752	0.871	0.0025	0.0195
50	2665	0.843	0.002	0.0198
60	2583	0.817	0.0017	0.0202
70	2504	0.792	0.0014	0.0205
80	2433	0.77	0.00125	0.0208
90	2363	0.748	0.0011	0.0211
92	2338	0.74	0.00109	0.0211

[a] In theory, the water/$NaNO_3$ content ratio of pure water tends to infinity. For practical purposes, the value used in the calculations for pure water (activity 1) has been extrapolated from the water/$NaNO_3$ content ratios obtained for the chemical activities equal to 0.982 and 0.965.

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