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Ageing of EUROBITUM bituminised radioactive waste: An ATR-FTIR spectroscopy study

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ABSTRACT

The extent of the physico-chemical processes of concern in the study of the acceptability of Eurobitum bituminised radioactive waste for underground disposal (water uptake by hygroscopic $NaNO_3$ – swelling – pressure build-up – $NaNO_3$ leaching) will depend on the degree of ageing of the bituminous matrix. In the work reported here, the ageing behaviour was studied by comparing the characteristics of 25 years old radioactive Eurobitum with those of 25 years old non-radioactive Eurobitum samples that were heated or gamma-irradiated in the presence or absence of oxygen. Chemical changes in the bitumen structure were followed in the mid-infrared region with Attenuated Total Reflectance Fourier Transform InfraRed Spectroscopy (ATR-FTIR) by measuring the evolution of the band heights at 1700 cm^{-1} (C═O functional groups) and 1600 cm^{-1} (C═C double bonds). Needle penetration depths and ring and ball softening points were determined for some samples. Oxidation of bitumen in the presence of oxygen results in a distinct increase of both the number of C═O and C═C functionalities, with a positive linear relationship existing between the two groups. The production of C═O functional groups seems to promote the generation of C═C double bonds. Heating at 130 °C is much more efficient than gamma irradiation at low to moderate dose rates (20–140 Gy/h) to oxidise the bitumen. As the oxygen concentration decreases, for instance by diffusion limitation deeper inside the bitumen, the number of C═O and C═C functionalities formed per unit of time decreases. A similar behaviour was observed for 25 years old radioactive Eurobitum. In absence of oxygen, gamma irradiation still results in a small increase of the number of C═O functional groups, probably by oxygen still adsorbed on the bitumen, and in a relatively higher amount of C═C double bonds. The surface layer (<5 cm) of 25 years old radioactive Eurobitum was heavily oxidised. The material had become very hard and brittle, and was full of small fissures. Due to these fissures, radio-oxidation processes took also place deeper inside the waste. The consequences of these observations for the long-term behaviour of Eurobitum in underground disposal conditions are discussed.

1. Introduction

Since the late sixties, bitumen has been widely used as a matrix for the immobilisation of low and intermediate-level radioactive waste, amongst others because of its good binding capacity, its low solubility in and low permeability to water, and its good chemical and biological inertia. Eurobitum bituminised radioactive waste has been produced by the EUROCHEMIC/BELGOPROCESS reprocessing facility (Mol-Dessel, Belgium) for the incorporation of precipitation sludges originating from the chemical reprocessing of spent nuclear fuel. With its total volume of ~3000 m^3 (containing ~3000 ton of waste) and its high specific alpha and beta–gamma activities (0.1 GBq/kg and 10 GBq/kg, respectively), it is a very important intermediate-level waste form in Belgium. An important feature of Eurobitum is that besides the ~60 weight% (wt%) of 'blown' (or: 'hard', 'oxidised') bitumen Mexphalt R85/40, it contains 25–30 wt% of $NaNO_3$, 4–6 wt% $CaSO_4$, and 0.5–1 wt% residual water. The waste further contains CaF_2, $Ca_3(PO_4)_2$, $Ni_2[(Fe,Mn)(CN)_6]$, and (hydr)oxides of Fe, Zr, and Al. The total radionuclide inventory (U and Pu isotopes, ^{241}Am, ^{244}Cm, ^{60}Co, ^{90}Sr, ^{137}Cs, . . .) is lower than 0.2 wt% [1,2].

The current reference solution pursued by the Belgian Agency for the Management of Radioactive Waste and Fissile Materials (ONDRAF/NIRAS) envisages the direct underground disposal of Eurobitum in a geologically stable clay formation [3,4]. Several 220-l drums would be grouped in cement-based secondary containers, which in turn are to be placed in concrete-lined disposal galleries that are excavated at mid-depth in the clay layer. The Boom Clay, which is a 30–35 million years old and ~100 m thick marine sediment, is presently being studied as a reference host formation. The physico-chemical properties of this plastic clay are interesting for radioactive waste disposal. The fine homogenous pore structure in combination with the low hydraulic conductivity [$(2–4) \times 10^{-12}$ m/s] ensures that the solute transport through the

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formation is essentially controlled by diffusion. The slightly alkaline pH (8.2–8.6) and reducing conditions ($E_{SHE} \sim -270$ mV or lower) imply a very low solubility for many radionuclides, and the high sorption capacity of the solid phase results in very low pore water concentrations for most radionuclides [3–5]. This results in an efficient retardation of the radionuclide migration. The Boom Clay will thus delay and spread in time the migration of the radionuclides, allowing the majority to decay before reaching the aquifers.

Owing to the importance of the clay host formation in the overall repository safety, it is important to verify whether the processes induced by the emplacement of Eurobitum will significantly affect the retardation properties of this barrier. The Belgian research program therefore focuses on the compatibility of Eurobitum with the Boom Clay, i.e. on the processes that might disturb the performance of the host formation. Basically, two types of disturbance can be distinguished [2,6]:

1. a mechanical disturbance, caused by the increase of the pressure in and around the waste, (a) due to the uptake of water by the dehydrated hygroscopic salts embedded in the waste, and (b) due to gas generation by anaerobic corrosion of the steel drums, radiolysis, and microbial activity.
2. a chemical disturbance (a) by the release of large amounts of $NaNO_3$ and other soluble salts, and (b) by the release of water-soluble organic potentially complexing compounds stemming from the radiolytic and chemical degradation of the bitumen.

The extent of some of these processes will be affected by the continuous evolution of the rheological properties of the bitumen in the bituminised waste, the so-called ageing [7–14]. This ageing results in harder bitumen, which tends to loose its binding capacity and which becomes increasingly brittle. A good understanding of bitumen ageing is thus essential for the study of the long-term behaviour of bituminised waste in geological disposal conditions.

2. Ageing of bitumen

2.1. Bitumen [7–14]

Bitumen is a complex mixture of molecules of a predominantly hydrocarbon nature (90–95 wt%). The three principal types of molecules are aliphatics (paraffinics or alkanes), naphtenics (naphthenes or cycloalkanes), and aromatics. Besides carbon and hydrogen, bitumen compounds contain also minor amounts of heteroatoms (S, N, O) – replacing carbon atoms in the bitumen molecules – and trace quantities of metals (V, Ni, Fe, Mg, Ca), occurring as inorganic salts and oxides [7,10]. Nearly all heteroatoms are bound to aromatic structures. The bitumen constituents can be divided into two broad chemical groups, the maltenes and the asphaltenes. The maltenes can be further subdivided in saturates, aromatics, and resins. The main characteristics of these four so-called SARA classes (Saturates, Aromatics, Resins, Asphaltenes) are summarised in Table 1.

The physical and chemical behaviour of bitumen is strongly affected by the way in which its compounds interact with one another. The molecules are held together through chemical bonds that are relatively weak and that can be broken by heat and/or shear forces. The weak chemical bonds are mainly electrostatic forces due to the heteroatoms, and hydrogen bonds, and to a lesser extent intermolecular Van der Waals interactions of long-chain hydrocarbons. Different models were proposed to describe the structure of bitumen. Probably the most common one – the SOL–GEL model – considers bitumen to be a colloidal system consisting of high molecular weight asphaltene micelles dispersed or dissolved in a lower molecular weight oily medium made up by the maltenes [7,10]. The micelles are considered to be asphaltenes together with an absorbed layer of resins, which act as a stabilising solvating layer to peptise the asphaltenes within the solvent phase. Away from the centre of the micelle there is a gradual transition to less polar aromatic resins and, finally, to a less aromatic oily dispersion medium. The relative amount of asphaltenes and the degree to which they are peptised considerably influence the viscosity of the bitumen. So-called 'solution' or 'SOL' type bitumens have sufficient quantities of resins and aromatics of adequate solvating power to fully peptise the asphaltenes, giving the micelles good mobility within the bitumen. 'Gelatinous' or 'GEL' type bitumens contain less resins and aromatics, or these compounds have insufficient solvating power: the micelles cannot be sufficiently well peptised, and the asphaltenes can associate to form large agglomerations or even a continuous network throughout the bitumen. In practice, most bitumens are of intermediate character.

2.2. Ageing of bitumen

It is well-known that the rheological properties of bitumen change with time [7–14], a phenomenon which is called ageing. As bitumen ages, it becomes harder, less plastic and – when molten – more viscous. In case of extreme ageing, it tends to loose its binding capacity, i.e. it becomes less adhesive and more cohesive, and it becomes increasingly brittle. The extent and rate of this ageing depend on many factors like chemical composition and structure of the bitumen, time, temperature, radiation, exposure to oxygen, etc. The main ageing process is an irreversible one, and is characterised by chemical changes of the bitumen [7,13]. Oxidation is the most important process in this type of ageing. Loss of volatile organic compounds and exudation (transfer of oily constituents from the bitumen into the embedded salts and (hydr)oxides) also contribute to the hardening. The second ageing mechanism is a reversible process called physical hardening [7,13]: it is attributed to the reorientation of bitumen molecules and the slow recrystallisation of waxes.

Oxidation of bitumen can be understood through the radical polymerisation scheme [8,11], which can be split up in three

Table 1
The main characteristics of the four SARA classes [7,10,11,13].

	Saturates	Aromatics	Resins	Asphaltenes
Wt% in bitumen	5–15	50–70	10–25	5–25
Wt% of heteroatoms	–	2–3 (S)	1 (N), 1 (O), 3-8 (S)	higher than in the resins
Basic hydrocarbon structures	straight and branched N–alkanes, cycloalkanes	cycloalkanes + $\sim$30% of C is included in aromatics	aromatics	aromatics
Molecular weight	300–2000	300–2000	500–50 000	1000–100 000[*]
Polarity	non-polar viscous oils	weakly polar	very polar	highly polar
Ratio C/H (aromaticity)	$\sim$0.5	$\sim$0.7	0.6–0.7	0.8–1.04

[*] Asphaltenes tend to associate together to form micelles with a molecular weight between 20 000 and 1 000 000.

steps. The first stage (*initiation*) consists of the production of free radicals by homolytic decomposition of covalent bonds (reaction 1). This can be achieved by transferring enough energy to the bonds, for instance by increased temperature or by radiation such as ultra-violet (UV) or alpha–beta–gamma, i.e. radio-oxidation [11]). In the second stage (*propagation*), the highly reactive radicals can react with other active species such as oxygen or carbon radicals, whilst preserving radicals in the system (reactions 2 to 5). The third stage (*termination*) is the one when radicals react without new radicals being formed. All this can be pictured by the following scheme where R, R′ and R″ refer to different carbon structures:

Initiation:

$$RH \rightarrow R^{\cdot} + H^{\cdot} \tag{1}$$

Propagation:

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \tag{2}$$

$$RO_2^{\cdot} + R'H \rightarrow RO_2H + R'^{\cdot} \tag{3}$$

$$RO_2H \rightarrow RO^{\cdot} + OH^{\cdot} \tag{4}$$

$$RO^{\cdot} + R''H \rightarrow ROH + R''^{\cdot} \text{or } ROH^{\cdot} + R'' \tag{5}$$

Termination:

$$ROH^{\cdot} + R'O^{\cdot} \rightarrow R{=}O + R'OH \tag{6}$$

$$RO_2H + R'{-}S{-}R'' \rightarrow ROH + R'{-}S(O){-}R'' \tag{7}$$

$$R^{\cdot} + R'^{\cdot} \rightarrow RR' \tag{8}$$

The list of reactions in this scheme is not exhaustive as many other reactions are possible. From these reactions, one can conclude that oxidation can lead to the following phenomena.

(i) The insertion of oxygen, if present (see further below), into the carbon backbone (see Table 1). The newly formed oxygen-containing groups can be hydroxyl (C–OH), carbonyl (C=O), carboxylic (COOR), or sulfoxide groups (S=O). The oxygen insertion takes place in molecules with heteroatoms (N, O, S) or with chemically reactive carbon atoms such as benzylic carbon [11].

(ii) The de-hydrogenation of cycloalkanes and aromatisation (increase of the carbon-to-hydrogen ratio (see Table 1), formation of C=C bonds), with concomitant production of hydrogen.

(iii) The formation of inter- or intra-molecular covalent bonds (reticulation).

In terms of the SARA classes, the oxidation of bitumen (e.g. by blowing air through it) generally results in an increase of the asphaltene content and a decrease of the saturates and aromatics content, whereas the resin content remains substantially of the same order [7,13–15].

The insertion of oxygen depends on the oxygen availability in the bituminous matrix. For pure bitumen, free access to oxygen or oxygen bearing radicals is only possible at the surface. Deeper inside the bitumen, oxygen availability is limited by oxygen diffusion, resulting in a strong decrease of the degree of oxidation with depth [11]. However, on the basis of literature data [16–20], one might expect the situation to be different for a bituminised waste form such as Eurobitum, where alpha–beta–gamma irradiation of the embedded $NaNO_3$ could generate oxygen or O- radicals. Yet, an additional 'activation' step (heating or dissolution) seems to be needed to release the produced O_2 from the $Na(NO_3,NO_2)$ crystal lattice.

The oxidised groups show a greater polarity and tend to associate into micelles of heigher molecular weight through more and stronger interactions. As a result, the hardness and the viscosity of bitumen increase.

2.3. Consequences for the geological disposal of bituminised radioactive waste

From the discussion above, it is clear that the properties of a bituminised waste form will evolve with time. Ageing of bitumen results in harder bitumen, which tends to loose its binding capacity and which becomes increasingly brittle. This is confirmed by measurements on small samples of radioactive Eurobitum exposed during (only) 13 years at ambient temperature to normal air, which show the ring and ball softening point to increase from 101 to 118 °C, with the penetration depth decreasing from 2.0 to 1.1 mm [2]. Ojovan et al. reported a hardening and a 10–25% increase of the asphaltene content of a $NaNO_3$ rich intermediate-level bituminised waste form that was stored in a shallow-ground repository for (only) 12 years [15]. External gamma irradiation of pure bitumen Mexphalt 15, at 10 kGy/h, to a total absorbed dose of 10 MGy, under a partial pressure of oxygen of 775 mbar, resulted in an increase of the asphaltene content of 17–55% [21]. As the asphaltenes contain more hydrophilic groups, an increased asphaltene content affects the affinity for water, and hence the water uptake and $NaNO_3$ leaching properties, of the aged bitumen.

The properties of the Bituminised Waste Product (BWP) that will come in contact with water within a few tens to hundreds or even thousands of years (depending on the type of host formation and the disposal concept), and that subsequently will slowly hydrate over a period of several thousands to tenthousands of years, will thus in no way be similar to the properties of the BWP at its production stage. Fissures and changes in membrane properties of bitumen (due to an increased asphaltene content) in terms of oxygen and water diffusion are expected to favour, during interim storage, the penetration into the BWP of oxygen – thus amplifying the ageing deeper inside the product – and, during geological disposal, of near field pore water – thus also possibly amplifying the ageing deeper inside the product (due to the presence of radiolytically produced oxygen bearing radicals). As a consequence, ageing might affect the extent of swelling and pressure increase due to uptake of water, as well as the related leaching of $NaNO_3$ and radionuclides.

We report here the results of a study on the ageing of Eurobitum including ~25 years old radioactive and non-radioactive Eurobitum samples. Non-radioactive Eurobitum was submitted to accelerated ageing treatments (heating or gamma irradation) in the presence or absence of oxygen. Chemical changes in the aged bitumen were followed using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR). For some samples, also the needle penetration depth [ASTM Procedure D 5-97] and the ring and ball softening point [ASTM Procedure D 36-95] were determined. The results were compared with the results for 25 years old radioactive Eurobitum sampled from an industrially produced drum. A second major objective of this study was to develop a method to produce 'aged' non-radioactive BWP samples with properties that resemble those of the 'aged' BWP in geological disposal conditions, for further use in water uptake experiments [22].

3. Experimental aspects

3.1. Eurobitum samples

Non-radioactive reference Eurobitum was sampled from a drum '0-2 CR15/16' that was produced during the 'cold runs (CR)' of EUROCHEMIC's bituminisation installation in the late 1970s

Table 2
Characteristics of the Mexphalt R85/40 and Eurobitum samples used in this study.

Identification	Production date	% salts	% $NaNO_3$	% H_2O	Density (g/ml)
R85/40	1998	–	–	–	1.05
0-2 CR15/16	11/01/1977	38.9	28.5	0.39	1.31
2-2000	27/08/1981	40.6	29.6	0.67	1.33

The specific α and $\beta\gamma$ activity of the BWP in drum 2-2000 is 0.17 GBq/kg and 7.9 GBq/kg, respectively (values for 1981).

(Table 2). The production method and composition of this non-radioactive reference Eurobitum are entirely similar to that of the radioactive Eurobitum, except for the presence of the RNs. Both loose fragments (using a hammer and a chisel) and cylindrical specimens (using a purpose-built sampling tube with inner diameter of 52 mm) were sampled. Radioactive Eurobitum samples with reference composition were taken in 2005 from an industrial waste drum (identification code 2-2000, produced in 1981; Table 2) in a hot-cell adjacent to the interim storage facility at BELGOPROCESS (former EUROCHEMIC), using a sampling device that was designed for this purpose [23]. Two sets of four cores of 52 mm in diameter and 60–70 mm height each were taken on two central–diagonal positions, resulting per position in a total sampled depth of ~250 mm (depth limited by the length of the sampling tube). In addition to the bitumen-salts mixtures, we included in our studies also *pure Mexphalt R85/40,* sampled from the batch that was used in the BELGOPROCESS bituminisation campaign of 1998–1999.

3.2. Accelerated ageing of Mexphalt R85/40 and non-radioactive reference Eurobitum

3.2.1. Heating

Heating is the most widely applied technique to study the ageing of bitumen. Several standard methods are frequently used, such as the Thin Film Oven Test [TFOT, ASTM D 1754-79] and the Rolling Thin Film Oven Test [RTFOT, ASTM D 2872-79]. As these techniques are not suited to prepare large volumes of aged bituminised waste, and as the expected degree of ageing was believed to exceed the ageing degree normally studied for road bitumens, we started simple heating experiments with thin layers of bitumen in contact with air at normal pressure. Thin layers of Mexphalt R85/40 and non-radioactive reference Eurobitum '0-2 CR15/16' were obtained by spreading the pre-heated material on a teflon plate and pressing it with a second, thicker teflon plate to the desired thickness of ~3 mm. The Eurobitum sample was first homogenised by heating during 60 min at 130 °C and regular mixing with a spoon. ATR-FTIR analysis showed that the additional oxidation of such mixed batches of Eurobitum is limited in comparison with the oxidation observed for thin layers. After cutting, the obtained sub-samples were exposed to air at 130 °C for durations up to 64 h. The oxidised surface of these sub-samples was analysed by ATR-FTIR, after pressing the samples to the pre-heated (10 min at 130–140 °C) ZnSe crystal (see below).

For the preparation of thermally aged Eurobitum for small scale water uptake experiments [22], 500 ml batches of crushed non-radioactive reference Eurobitum '0-2 CR15/16', placed in steel beakers of 80 mm diameter and 150 mm height, were heated at 180 °C and manually mixed to maximise the exposure of the bulk of the material to air. After 4 h of continuous mixing, the BWP became very viscous, and proper manual mixing in these small and high beakers became very difficult. Hence, the mixing was stopped and the material was allowed to cool down slowly to ambient temperature. In the initial stage of the cooling process, the sample was occasionally stirred to remove air bubbles formed at the bottom of the sample. From the cores of this thermally aged Eurobitum, obtained after removal of the steel beaker, cylindrical samples of 10 mm thickness were cut for later use in the water uptake tests [22]. Sub-samples were analysed by ATR-FTIR. For the preparation of thermally aged Eurobitum for a large-scale water uptake experiment, a large volume (~18 l; placed in a steel container of 420 mm in diameter and 300 mm height) of crushed non-radioactive reference Eurobitum 0-2 CR15/16 was first slowly heated to ~180 °C and subsequently mixed during 8 h with a manually manipulated electrically driven stirrer, to maximise the exposure of the bulk of the material to air. The bituminous mixture was then allowed to cool down slowly to ambient temperature. In the initial stage of the cooling process, the sample was occasionally stirred to remove air bubbles formed at the bottom of the sample. Next, the steel container was removed, and out of the ~150 mm heigh sample, several sub-samples were cut for further water uptake tests and for analyses. Part of the sub-samples were analysed by ATR-FTIR. Needle penetration depth and ring and ball softening point were determined as well.

3.2.2. External gamma irradiation

In radioactive Eurobitum, the total absorbed dose will essentially be due to the alpha emitters, the contribution of the beta/gamma emitters being essentially limited to the first 300 years [24]. Simulating the effects of internal alpha–beta–gamma radiation by external gamma radiation at higher dose rates has often been criticised not to simulate adequately damages caused by alpha particles [25]. If the direct effects of the gamma irradiation are similar in nature to those of alpha particles (ionisation, excitation), they differ strongly by the spatial repartition, the density of damages, and the yield of irradiation products. Kowa and co-workers, for instance, report a three times higher yield of radiolytically generated H_2 when bituminous samples are internally irradiated with alpha emitters, compared to external gamma irradiation [24]. However, on the basis of the homogeneous distribution of radionuclides in the BWP, and because the BWP samples in this study were gamma-irradiated from all directions, we assume a homogenous distribution of radiation effects (damages) throughout the BWP in both cases.

Non-radioactive samples of EUROBITUM and pure Mexphalt R85/40 were gamma-irradiated in the GEUSE-2 facility (Gamma Experiments Using Spent fuel Elements) in the BR2 reactor (SCK•CEN, Mol, Belgium), during 240 days [26]. Both ring shaped (inner and outer diameter 200 and 300 mm, height 10 mm; only Eurobitum) and rod shaped samples (diameter ~1 cm, length 8 cm; Eurobitum + Mephalt R85/40) were irradiated. The sample-holder consisted of six horizontal levels, each receiving a different dose rate. Dose rates were determined before and after the irradiation by means of certified dosimeters (Red Perspex Type 4034S, Harwell Dosimeters). The 95% uncertainty on the dose rate measurements is estimated to be ~10%. Dose rates were higher than in the industrially produced radioactive Eurobitum, and varied between ~20 and ~140 Gy/h, to deliver total absorbed doses between ~140 and ~750 kGy. Taking into account that for the hard (blown, oxidised) Mexpalt R85/40 the yield of radiolytically produced H_2 is about 3 times higher under alpha irradiation than under beta/gamma irradiation [24], the dose of ~750 kGy corresponds to the calculated alpha (~200 kGy) and beta-gamma (~100 kGy) dose absorbed by the BWP after about 200 years. Scoping calculations showed that for a disposal site in the Boom Clay the BWP would be in contact with pore water in less than 100 years after its disposal [27].

Three levels of the sample-holder were exposed to air, the other three were flushed continuously with nitrogen ($O_2 < 2 \times 10^{-4}$ vol.%) to avoid or minimise reactions with oxygen. During the irradiation, nitrogen pressure (1.2 bar), flux (~0.5 l per min), and temperature (20–35 °C) were regularly verified. The Eurobitum of the ring shaped samples irradiated under nitrogen was to be used in water uptake tests [22]. To preserve the internal structure of the BWP created by the irradiation (pores, cracks), samples were moulded before the irradiation by warming on a heating plate (~1 h, 80–100 °C) and subsequently pressing, in a glove-box that was flushed with nitrogen and that was equipped with an oxygen removal system ($O_2 < 1 \times 10^{-4}$ vol.%), to minimise the oxidation. Despite the low O_2 content in the glove-box, this treatment resulted in a very small oxidation of the surface of these samples (see Section 4).

3.3. Radioactive samples

Layers of ~3 mm thick were cut with a firmly stretched steel wire from the top and/or bottom of four cores (diameter 52 mm, length 60–70 mm) of the radioactive Eurobitum (the central part of the cores was reserved for water uptake tests). Each of the 3 mm slices was then further subdivided in two lamellar samples of ~15 mm width and 40–50 mm length (duplicate samples). The (initially inner) surface of these samples was then placed on the pre-heated (30 min at 140 °C) ZnSe crystal for ATR-FTIR analysis (see below). The presence of radioactive elements in the sample had no effect on the FTIR spectra.

3.4. Characterisation of bitumen and Eurobitum

Bitumen is a viscoplastic material with properties that are very much dependent on temperature, and with no clearly defined melting temperature. Hence, in the more common bitumen characterisation methods (needle penetration depth and ring and ball softening point), temperature is a very important factor. The instructions for these characteristics need to be strictly followed, which is not always obvious. In addition, these methods are not always suited to characterise intermediate-level BWPs. The presence of harder salt crystals and sometimes air-filled pores yields a high variability of the penetration depth measured on such samples [28]. The relatively high activity of radioactive samples raises some problems (high radiation doses, risk of contamination, large amounts of secondary radioactive waste) that can be partly overcome by implementation of expensive measures. Finally, these 'physical' methods do not yield 'chemical' information. Therefore, we opted for Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) to characterise the (ageing) of bitumen and Eurobitum.

Owing to its sensitivity and exploiting ease, Fourier Transform InfraRed Spectroscopy in the mid-infrared domain (4000–400 cm^{-1}) has been a major analytical technique to study the ageing mechanisms in asphalt, through the characterisation of oxygen-containing functional groups and hydrocarbon groups (e.g. [11–13]). Absorption bands in the range of 4000–1500 cm^{-1} are typically due to functional groups (e.g. –OH, C=O, N–H, CH_3, etc.). Absorption bands in the region between 1500 and 400 cm^{-1}, referred to the fingerprint region, are generally due to bending vibrations within the molecule, and are highly specific for each material. The major mid-infrared absorption frequencies of bitumen are shown in Table 3. The untreated ATR-FTIR spectra of pure Mexphalt R85/40 and of the non-radioactive reference Eurobitum are shown in Fig. 1. It is seen that in Eurobitum the spectrum of the Mexphalt R85/40 is strongly influenced by the presence of nitrates and sulphates. $NaNO_3$ (~28 wt% of the waste) has a strong band at 1380–1350 cm^{-1}, coinciding partially ('shoulder') with the $–CH_3$ (symmetric bending) band, and a narrow band at 835 cm^{-1}, coinciding with the –CH band. Sulphate (5 wt% of the waste) gives a large band between 1300 and 1000 cm^{-1}, hiding the S=O band at 1030 cm^{-1}. The broad band at 3650–3100 cm^{-1} in the spectrum for Eurobitum could not be identified. Oxidation of bitumen results a.o. in an increase of the absorbance at 1700 cm^{-1} (C=O stretch in carbonyl compounds) and 1600 cm^{-1} (C=C stretch in carbon carbon double bonds). It leads also to an increase of the sulfoxide (S=O) functional groups at 1030 cm^{-1}, but because of the large band of sulphates, this was not considered in our study. Also the spectral changes in the region of 3400–3100 cm^{-1} – with hydroxylic functional groups – could not be interpreted satisfactorily, and were therefore not considered.

Traditional FTIR implies first dissolution of the sample in a solvent such as di- or trichloromethane or carbon disulfide, followed by a filtration step if the bitumen matrix is loaded with particles that can interfere with the infrared radiation. For Eurobitum, with up to 40 weight% of salts and (hydr)oxides, the filtration was shown to be impossible due to the rapid plugging of the filters, and would, in the case of radioactive Eurobitum, have generated a lot of secondary waste and risks on contamination. ATR-FTIR overcomes these problems. This analysis technique is based on the evanescent wave phenomenon, where a beam of electromagnetic radiation is internally reflected by means of an internal reflection element (IRE) such as a zinc selenide (ZnSe) crystal, which is infrared transparent and which has a high refractive index. Almost no sample preparation is required, as spectra are obtained by pressing thin layers of bitumen against a pre-heated internal reflection element. The depth of penetration of the evanescent wave in the bituminous sample is typically 2–3 μm. The IRE window made of ZnSe used in our study is 1 cm wide and 7 cm long (used with the Bruker Vector22 spectrometer). It is important that the sample covers completely the window surface, thus avoiding spaces filled with the infrared-absorbing atmospheric gases

Table 3

Mid-infrared absorption frequency ranges of the major stretching (υ), bending (δ), and out-of-planes bending (γ) frequencies of bitumen in the region of interest [12,29,30]. ⟨⟨ *sp*2 ⟩⟩ and ⟨⟨ *sp*3 ⟩⟩ mean that the carbon atoms are *sp*2-hybridised (=CR–H) and *sp*3-hybridised (R_3C–H), respectively.

Chemical groups	Vibrational modes	Range (cm^{-1})	Maximum (cm^{-1})
–OH	Stretching *v*	3400–3100	3270, 3180
–CH *sp*2	Stretching *v*	2970–2940	2955
X–CH_3, aryl–CH_3	Stretching *v*	2910–2870	2880
(–CH_2, –CH_3) sp3	Asymmetric stretching	2900–2820	2865
(–CH_2, –CH_3) sp3	Symmetric stretching	2850–2800	2815
–C=O	Stretching *v*	1753–1635	1700
–C=C–	Stretching *v*	1635–1538	1600
–CH_2, –CH_3	Bending (asymmetric) δ	1538–1399	1460
–CH_3	Bending (symmetric) δ	1399–1349	1376
–S=O	Bending δ	1082–980	1030
–C=CH– when 1 H singlet	Out-of-planes bending of H atoms γ	910–837	864
–C=CH when 2–3 H adjacent	Out-of-planes bending of H atoms γ	837–780	800
–C=CH when 3–4 H adjacent	Out-of-planes bending of H atoms γ	775–731	743
$(CH_2)_n$	Rocking	731–705	722

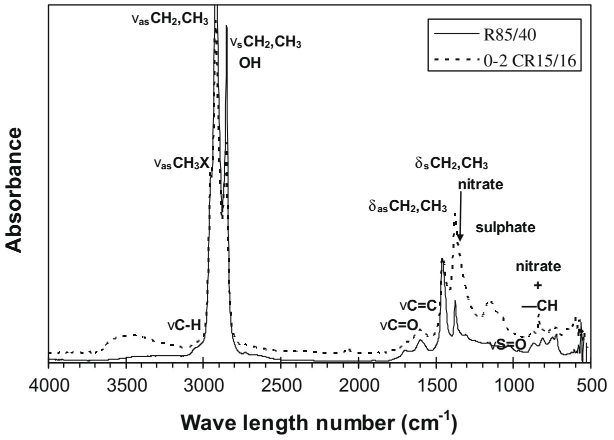

Fig. 1. ATR-FTIR raw (i.e. untreated) absorbance spectra of Mexphalt R85/40 and of non-radioactive reference Eurobitum 0-2 CR15/16.

CO_2 and H_2O. Measurements were also done with a 'Golden Gate' ZnSe crystal with a scanning surface of a few mm^2 only. However, because of the presence of salt crystals and hydr(oxides) of varying size (1–100 μm), the variability of the results obtained this was unacceptably high.

For the interpretation of the FTIR spectra, we adopted a procedure that is used by the Belgian Road Research Centre [A. Verhasselt, BRRC, personnal communication]. First, the absorbances are recalculated in function of those at ~1885 cm^{-1} and at ~1460 cm^{-1}, which are set arbitrarily at 0 and 1.2, respectively. These two wavelength numbers correspond with the minimum and the maximum absorbances in the region comprising 1700 cm^{-1} (C=O) and 1600 cm^{-1} (C=C). The absorbances at ~1885 cm^{-1} and at ~1460 cm^{-1} proved to be independent of the degree of oxidation, and not to be much influenced by small variations of the salt content (Fig. 1). After this normalisation, the baseline between 1885 cm^{-1} and 686 cm^{-1} is subtracted. These two wavelength numbers were chosen in our study because the corresponding absorbances were shown not to vary with the oxidation of the bituminous matrix. The normalised spectra of the raw spectra of Fig. 1 are shown in Fig. 2.

A validation program has shown that the height of the peaks of the IR absorbances at 1700 cm^{-1} and 1600 cm^{-1}, referred to as H1700 and H1600, respectively, can be used as ageing indicators (Fig. 3). The relative uncertainty on these values for well mixed (homogeneous) samples is ~10% (95% confidence). For samples taken from different positions within one drum or between drums produced from the same batch, uncertainties are 20% (H1700) to 30% (H1600) (95% confidence). This higher uncertainty is probably due to differences in degree of oxidation of the 25 years old Eurobitum, depending on the position of the sample in the drum (close to surface *versus* deeper inside the BWP).

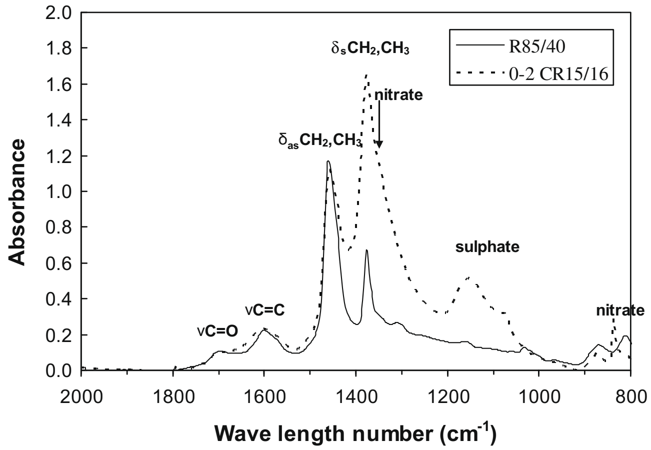

Fig. 2. Normalised ATR-FTIR spectra (region of interest) of Mexphalt R85/40 and non-radioactive reference Eurobitum 0-2 CR15/16.

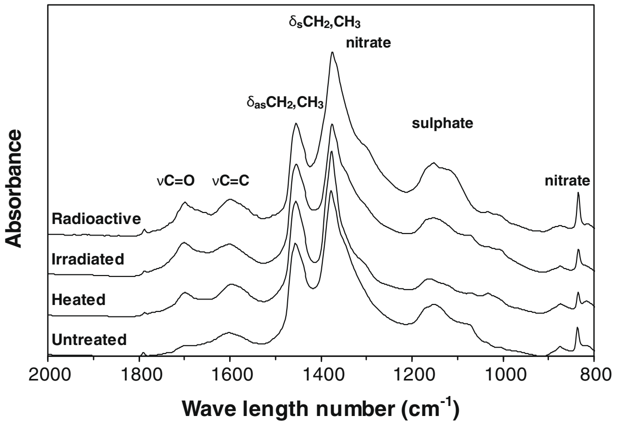

Fig. 3. Normalised ATR-FTIR spectra of different Eurobitum samples. An untreated reference sample 0-2 CR15/16 is compared with a reference sample heated in air at 130 °C for 16 h, with one having absorbed a dose of 0.73 MGy of gamma radiation in contact with air, and with one sampled from the upper layer of radioactive Eurobitum (drum 2-2000) that was produced in 1981.

For some of the non-radioactive samples, the needle penetration depth and the ring and ball softening point were measured as well. Our test conditions for those measurements were kept unchanged as much as possible, but they deviate slightly from the guidelines of the American Society for Testing and Materials. For instance, penetration depths were measured directly on the irradiated samples (at 25 °C). In case of the ring and ball softening point, the steady temperature increase of 5 °C per min could not always be strictly followed over the whole temperature range.

4. Results and discussion

4.1. Heating (in the presence of oxygen)

Fig. 4 shows the results of exposing thin layers of pure Mexphalt R85/40 and Eurobitum 0-2 CR15/16 to air at 130 °C. Both the values for H1700 (C=O) and H1600 (C=C) increase with the duration

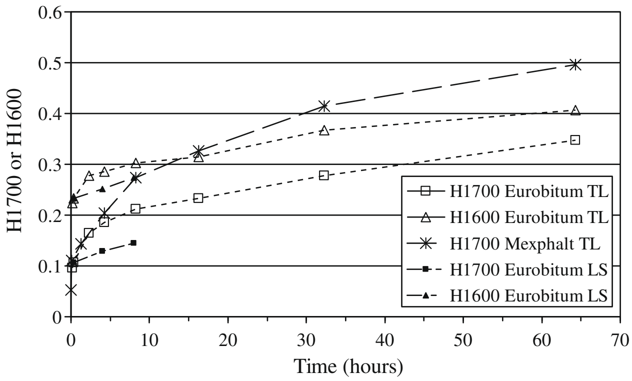

Fig. 4. Evolution, with exposure time, of H1700 and H1600 values for thin layers (TL) of Mephalt R85/40 and Eurobitum 0-2 CR15/16 in contact with air at 130 °C. The evolution of the H1600 values for thin layers of Mexphalt R85/40 was very similar to that of Eurobitum 0-2 CR15/16 (△), and is omitted for clarity. The H1700 and H1600 values for larger samples (LS) of Eurobitum, mixed during 4 and 8 h at a temperature of 180 °C, are also included in the graph.

of the exposure to high temperature in air, demonstrating the oxidation of the bitumen. An initial rapid raise of the H1700 and H1600 values is followed by a slower increase. After 64 h of heating, the H1700 (C=O) and H1600 (C=C) values for Eurobitum '0-2 CR15/16' were as high as 0.35 ± 0.04 and 0.41 ± 0.04, respectively, and still continued to increase. The respective values for the unheated material were 0.10 ± 0.01 and 0.23 ± 0.02. When plotted against the square root of time, a linear behaviour is observed (results not shown). Such behaviour is typical for diffusion controlled processes. It is likely that in a first phase the groups that are more easily accessible to O_2 and/or the more reactive groups are oxidised. The oxidation of groups or fragments that are less easily accessible to O_2 – because they are situated a little bit (2–3 μm) deeper inside the bitumen – and/or that are less reactive proceeds more slowly. As the amount of C=O functional groups increases, more carbon carbon double bonds are formed as well. It thus appears that reaction of bituminous compounds with oxygen promotes the formation of carbon carbon double bonds. This is discussed in detail further below.

The rapid increase of the H1700 and H1600 values during the 1st h shows that care should be taken when comparing the value of these parameters for short heating durations. It is also seen that the evolution of the H1700 values is different for the non-radioactive reference Eurobitum and the Mexphalt R85/40. This different behaviour is likely due to (i) the fact that the 'untreated' Mexphalt R85/40 was less oxidised than the 'untreated' Eurobitum (in which the Mexphalt R85/40 was additionally mixed during ~2 h at 150–190 °C with the waste slurry) and (ii) the fact that the Mexphalt R85/40 is not 'diluted' with 40 wt% (~15–20 vol.%) of salts and (hydr)oxides, such as in Eurobitum, which means that per unit of surface more C=O functional groups can be formed. This observation shows that we cannot quantitatively compare the results of Mexphalt R85/40 and Eurobitum. It is important to mention that the results for Eurobitum samples with waste contents varying by up to ~10% can be compared without difficulty.

The H1700 and H1600 values for larger samples (LS) of Eurobitum, mixed during 4 and 8 h at a temperature of ~180 °C – this is about 50 °C higher than for the thin layers – are also included in Fig. 4. Especially for the C=O functional groups, the H1700 values are considerably lower than the values for the thin layers. This shows that the 'effective' contact time with oxygen was considerably smaller than the total heating time. For the C=C functional groups, the difference with the values for the thin layers is systematically smaller. The formation of carbon carbon double bonds thus proceeds at least partially independently from the generation of C=O functional groups.

Besides the evidence of oxidation by the increase of the quantity of C=O and C=C functional groups, the heated samples also proved to be harder. The thin bitumen layers became hard and glassy; the penetration depth was not measured. With increasing exposure time, it became increasingly more difficult to apply the bitumen layers properly on the pre-heated ZnSe crystal. The needle penetration point of the Eurobitum that was heated and mixed in larger batches decreased from 1.78 mm (untreated) to 1.39 mm (4 h heating) and 1.21 mm (8 h heating). The ring and ball softening point increased from 123 °C for the untreated sample to 162 °C for the sample that was heated during 8 h (note that the softening point of untreated Mexphalt R85/40 is only 93 °C).

4.2. Gamma irradiation in the presence and absence of oxygen

One of the outcomes of the gamma irradiation was clear when the samples were retrieved from the irradiation container. The samples irradiated under nitrogen were, at least at first sight, not affected. The samples irradiated under air appeared clearly harder than before the irradiation.

For the ATR-FTIR analysis of Eurobitum irradiated under nitrogen, several sub-samples were taken from the outer rims of the three ring shaped samples, as well as of a non-irradiated control ring that was stored during 240 days at ambient temperature in

Table 4

H1700 (C=O) and H1600 (C=C) values measured on different samples of Eurobitum and pure Mexphalt R85/40. *n* refers to the number of measurements.

Treatment	Position	H1700	H1600	*n*
Eurobitum 0-2 Cr15/16				
'Untreated' (heat, 10', 110 °C, air; Fig. 5)[a]	Surface	0.094 ± 0.005	0.224 ± 0.006	6
Heat (140', 130 °C, air; Fig. 5)[b]	Surface	0.164 ± 0.016	0.277 ± 0.028	1
Heat (10', 80 °C, air) + irrad. (162 kGy, air)[c]	~3 mm	0.116 ± 0.024	0.222 ± 0.073	1
Heat (10', 80 °C, air) + irrad. (255 kGy, air)[c]	~3 mm	0.144 ± 0.028	0.251 ± 0.083	1
Heat (10', 80 °C, air) + irrad. (732 kGy, air)[c]	~3 mm	0.147 ± 0.030	0.251 ± 0.083	1
Heat (60', 80-100 °C, N_2)[d]	~3 mm	0.103 ± 0.007	0.235 ± 0.013	5
Heat (60', 80–100 °C, N_2) + irrad. (139 kGy, N_2)[d]	~3 mm	0.109 ± 0.004	0.242 ± 0.004	5
Heat (60', 80–100 °C, N_2) + irrad. (338 kGy, N_2)[d]	~3 mm	0.108 ± 0.006	0.252 ± 0.007	4
Heat (60', 80–100 °C, N_2) + irrad. (770 kGy, N_2)[d]	~3 mm	0.110 ± 0.009	0.233 ± 0.008	4
Irrad. (960 kGy, air)	Surface	0.434 ± 0.087	0.344 ± 0.103	1
Irrad. (960 kGy, air)	Surface	0.226 ± 0.045	0.291 ± 0.087	1
Irrad. (960 kGy, air)	Surface	0.304 ± 0.061	0.315 ± 0.095	1
Irrad. (960 kGy, air)	Surface	0.263 ± 0.053	0.307 ± 0.092	1
Irrad. (960 kGy, air)	Surface	0.331 ± 0.066	0.316 ± 0.095	1
Irrad. (960 kGy, air)	~5 mm	0.119 ± 0.024	0.249 ± 0.075	1
Irrad. (960 kGy, air)	~5 mm	0.124 ± 0.025	0.249 ± 0.075	1
Mexphalt R85/40				
'Untreated' (heat, 10', 80 °C, air)[a]	Surface	0.096 ± 0.014	0.193 ± 0.017	3
'Untreated' (heat, 10', 110 °C, air; Fig. 5)[a]	Surface	0.110 ± 0.012	0.234 ± 0.023	7
Heat (260', 130 °C, air; Fig. 5)[b]	Surface	0.204 ± 0.020	0.260 ± 0.052	1
Heat (10', 80 °C, air) + irrad. (162 kGy, air)[c]	~3 mm	0.151 ± 0.030	0.235 ± 0.071	1
Heat (10', 80 °C, air) + irrad. (255 kGy, air)[c]	~3 mm	0.153 ± 0.031	0.239 ± 0.072	1
Heat (10', 80 °C, air) + irrad. (732 kGy, air)[c]	~3 mm	0.168 ± 0.034	0.203 ± 0.061	1
Heat (10', 80 °C, air) + irrad. (139 kGy, N_2)[c]	~3 mm	0.096 ± 0.019	0.228 ± 0.068	1
Heat (10', 80 °C, air) + irrad. (338 kGy, N_2)[c]	~3 mm	0.102 ± 0.020	0.207 ± 0.062	1
Heat (10', 80 °C, air) + irrad. (770 kGy, N_2)[c]	~3 mm	0.094 ± 0.019	0.203 ± 0.061	1

[a] These samples were heated 10 min at 110 °C to cover the ATR crystal.

[b] The sample was first mixed and spread as a thin layer on a Teflon plate (see Fig. 5).

[c] Bar-shaped samples were prepared by small heating (melting) of the starting samples.

[d] The ring was heated on a heating-plate (~1 h, 80–100 °C) in a glove-box under nitrogen atmosphere ($O_2 < 1 \times 10^{-4}$ vol.%).

a nitrogen atmosphere ($O_2 < 1 \times 10^{-4}$ vol.%). The spectra were all very similar, and very comparable to the spectrum of the starting sample, independently of the total absorbed dose. The average H1700 and H1600 values are summarised in Table 4. Careful examination of the data reveals that the values for the four rings are slightly higher than the values of the 'untreated' starting sample. This is probably due to a small oxidation during the preparation of the rings (60 min at 80–100 °C; $O_2 < 1 \times 10^{-4}$ vol.%) to mould the rings, by oxygen still adsorbed on the surface of the starting material. It is further seen that the values for the gamma-irradiated rings are statistically not different from the values for the non-irradiated control ring. These results demonstrate that radiolytic decomposition of nitrates as a source of oxygen for the oxidation of the bituminous matrix [16–20], did not take place. This is not unexpected, since the oxygen that is produced from the irradiation of $NaNO_3$ remains trapped in the $Na(NO_2,NO_3)$ crystal lattice until the crystal is heated or dissolved. Furthermore, it is observed that the scission and recombination reactions under gamma irradiation in absence of oxygen and at low to moderate dose rates do not generate a high amount of carbon carbon double bonds. During the irradiation of bitumen, existing carbon carbon double bonds are destroyed whilst at other places new double bonds are formed. It would be very coincidental if for all three irradiated rings, with different total absorbed doses under different dose rates, the amount of carbon carbon double bonds would have stayed almost constant. It thus appears again that the production of carbon carbon double bonds is, at least partially, triggered by the generation of C═O groups.

The needle penetration depths measured for the non-irradiated ring and for the ring irradiated under nitrogen until 770 kGy were similar, 1.78 mm and 1.83, respectively. Ring and ball softening points of non-irradiated and irradiated samples were in the range 126–128 °C, which is, taking into account the slight oxidation during the preparation of the samples, very similar to the value of 122 °C for the starting material. All these results indicate that the gamma irradiation in the absence of oxygen has not caused an important oxidation of the bitumen. Samples that were gamma-irradiated in the absence of oxygen until a total absorbed dose of 0.77 MGy were used in water uptake experiments in confined (constant volume) and semi-confined (constant stress) conditions [22]. The evolution of the swelling (constant stress) or swelling pressure (constant volume) was the same as for unirradiated control samples, showing that irradiation in absence of oxygen indeed does not change much the properties of the bituminised waste towards uptake of water and release of $NaNO_3$. Similar results were obtained for the bar-shaped Mexphalt R85/40 samples (Table 4).

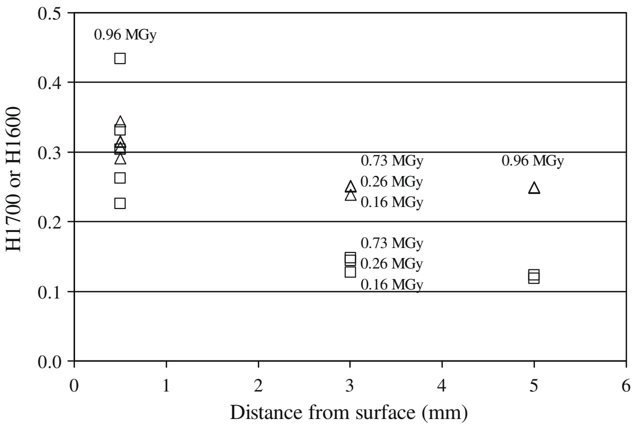

Fig. 5. Decrease of H1700 (C═O; □) and H1600 (C═C; △) values with distance from the surface of Eurobitum 0-2 CR15/16 samples that were gamma-irradiated under air at different dose rates and total absorbed doses. Total absorbed doses were obtained at dose rates of 140 Gy/h (0.96 MGy), 128 Gy/h (0.73 MGy), 45 Gy/h (0.26 MGy), and 20 Gy/h (0.16 MGy). The uncertainty on the distances is approximately 0.5 mm.

For the Eurobitum samples irradiated under air, both the surface and the interior part (~3 or ~5 mm) was analysed by ATR–FTIR. The results are graphically shown in Fig. 5. It is seen that both the H1700 (C═O) and H1600 (C═C) values decrease rapidly with depth. Since at ambient temperature the gamma irradiation of $NaNO_3$ inside the BWP was shown not to produce oxygen available for bitumen oxidation, and as the availability of oxygen or O-radicals decreases as a function of depth due to diffusion limitation [11], this behaviour could be expected. The reaction of O-radicals with reactive bitumen compounds additionally immobilises oxygen in the outer layer, increasing the O_2 concentration gradient within the bitumen. The data for the surface (in the graph set at a distance of 0.5 mm from the surface) show a large scatter, especially for the H1700 (C═O) values. This is the result of the fact that the surface of the gamma-irradiated samples was rough, and that this roughness was different for the 5 studied samples. The larger the roughness, the higher the 'effective' surface for reaction with oxygen, and the higher the degree of oxidation of the smoothed layer (obtained after application on the pre-heated ZnSe crystal) that is finally scanned during the ATR-FTIR analysis. The values for 3 and 5 mm are very similar, although they were obtained for different total absorbed doses, at different dose rates. Thus, at distances of ~3 mm from the surface, the very low O_2 concentration is the limiting factor for radio-oxidation. Values at 5 mm are nearly the same as the values for Eurobitum irradiated in the absence of oxygen (Table 4).

The data at ~3 mm in Fig. 5 were obtained for different dose rates (20–45–140 Gy/h) and different total absorbed doses (0.16–0.26–0.73 MGy). These values are presented in Fig. 6 as a function of the total absorbed dose. Although differences are small, it is seen that both the H1700 and H1600 values first increase with absorbed dose, until an absorbed dose of ~0.3 MGy. Thus, beyond a given dose rate – which (for Eurobitum) at a depth of ~3 mm seems to be around 45 Gy/h – oxygen availability becomes the oxidation rate limiting factor. Below this 'threshold' dose rate, the concentration of highly reactive radicals becomes the limiting factor for radio-oxidation (i.e. dose rate dependence). Closer to the surface, where the oxygen concentration is (normally; but this depends also on the dose rate [11]) higher, the 'threshold' dose rate is also higher. This behaviour is in agreement with the results reported by Walczak [11].

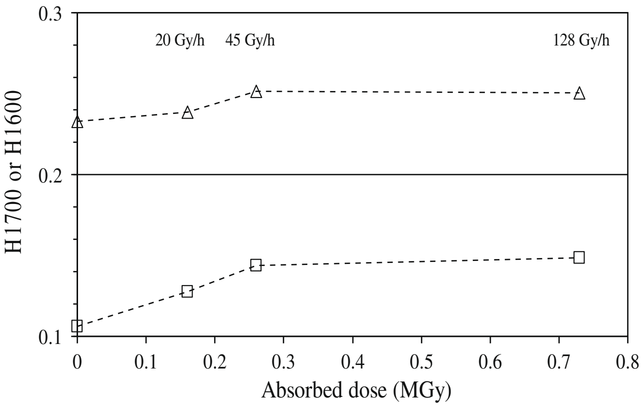

Fig. 6. H1700 (C═O; □) and H1600 (C═C; △) values measured at a distance of ~3 mm from the surface of non-radioactive Eurobitum 0-2 CR15/16 that was gamma-irradiated during 240 days at different dose rates.

4.3. Radioactive samples

During the manipulation of the radioactive Eurobitum to obtain thin slices for ATR-FTIR analysis, it appeared that the upper layer of the upper cylindrical sample (height of ~6 cm) was heavily oxidised. When cutting the upper ~10 mm layer of this sample with a firmly stretched steel wire, the loaded part of the sample disintegrated nearly completely into small crumbles. The surface layer of the radioactive Eurobitum had thus become very hard, brittle, and full of (micro-)fissures. It can be expected that such hardened and fissured Eurobitum will behave totally different when in contact with underground pore water. As the upper layer could not be used for ATR-FTIR analysis, we decided to cut a second thin layer, of which in this case the upper surface (closer to the surface of the Eurobitum) was analysed. Also this sample proved to be hard and full of fissures, and it took a lot of time and careful manipulation to apply the subsamples cut from this thin layer properly on the ZnSe crystal for ATR-FTIR analysis. The cutting of sub-samples from the deeper cylindrical samples (6–12, 12–18, and 18–24 cm from the surface) was easier.

Fig. 7 shows the evolution of the H1700 (C=O) and H1600 (C=C) values as a function of the distance of the sample from the surface of the 25 years old radioactive Eurobitum. The height of the bituminised waste in a 220 l drum that is filled for 85 vol.% with Eurobitum is ~75 cm. It is clearly seen that an upper layer of ~5 cm thickness is extremely oxidised. The H1700 value (0.35 ± 0.07) and H1600 value (0.35 ± 0.10) are about as high as the respective values for Eurobitum 0-2 CR15/16 that was heated during 64 h at 130 °C (contact with air), i.e. 0.35 ± 0.04 and 0.41 ± 0.04, respectively (Fig. 4, Table 4). The values then decrease – sharply in case of the C=O functional groups – with depth. Yet, the H1700 (>~0.15) and H1600 values (>~0.28) remain, at least until a depth of ~25 cm, higher than the values measured for the 25 years old non-radioactive reference Eurobitum (i.e. 0.10 and 0.23, respectively). The values are also (slightly) higher than the values at a depth of 3 and 5 mm in inactive Eurobitum samples that were gamma-irradiated in the presence of oxygen, at higher dose rates and during only ~150 days (Fig. 5). Radio-oxidation involving the reaction with oxygen thus took place to a depth of at least ~25 cm. Extrapolation of the data suggests that this oxidation occurred also deeper in the drum, but is impossible to estimate to what depth.

At present, the source of oxygen or O-radicals deeper in the BWP remains uncertain. Two processes can be considered. First, and this is the more likely process, oxygen may have penetrated deeper in the Eurobitum by diffusion from the surface. The dose rates in an intermediate-level radioactive waste form such as Eurobitum (0.1–0.5 Gy/h alpha, 1–10 Gy/h beta/gamma [11,24]) are sufficiently low to make the highly reactive organic radicals the rate limiting compounds, thus allowing the unreacted oxygen to diffuse deeper into the waste (cfr. Fig. 6 + related discussion). The slow but continuous development of a continuum of small fissures in the oxidising (hardening) layer facilitates the oxygen diffusion. The high variation of the results in the region 5–25 cm could then be explained by the combination of less oxidised material further away from fissures and more oxidised material closer to the fractures. We can expect that with time more fissures will be formed in the waste, in turn accelerating the diffusion rate of oxygen in the waste. Second, as already mentioned, also irradiation of $NaNO_3$ (~28 wt%) can lead to the production of oxygen or O-radicals. However, as already discussed, the irradiation of $NaNO_3$ – generating $NaNO_2$ and O_2 dissolved in the crystal lattice – has to be followed by an 'activation' step (heating, dissolution in water) in order to release the produced O_2 [16–20]. Our results learned that gamma irradiation of Eurobitum at ambient temperature did not result in the release of (high amounts of) oxygen. It is possible that, in analogy with the higher yield of radiolytically produced H_2 [24], alpha irradiation of $NaNO_3$ generates more oxygen than gamma irradiation, but it remains unclear whether in the case of alpha radiation this O_2 becomes available for reaction. As the nitrite concentrations in leachates from experiments with radioactive Eurobitum samples are very low (mostly below the detection limit; but this detection limit is relatively high because of the high concentrations of nitrate), the amount of $NaNO_2$ and O_2 produced by irradiation of $NaNO_3$ should be very low. We therefore conclude that the most important oxygen source is diffusion from the surface.

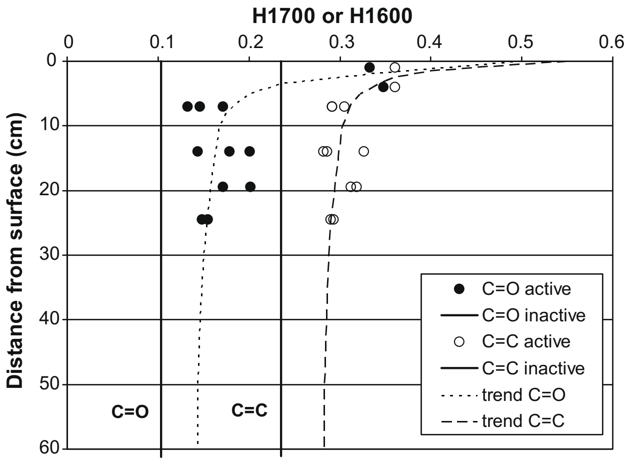

Fig. 7. Evolution of the H1700 (C=O) and H1600 (C=C) values as a function of the distance of the sample from the surface of the 25 years old radioactive Eurobitum.

For the C=C functional groups, we observe again slightly higher values for the samples for which the number of C=O functional groups had strongly increased, indicating that the formation of part of the carbon carbon double bonds is facilitated by the production of C=O functional groups. The ratio of C=C to C=O is, however, different from that of heated Eurobitum. This is elaborated in detail below.

4.4. C=O versus C=C

In this study, we have compared the H1700 (C=O) and H1600 (C=C) values of a 25 years old radioactive Eurobitum with the respective values of a 25 years non-radioactive Eurobitum that was either untreated or submitted to accelerated ageing by heating or gamma irradiation, in the presence or absence of oxygen. This resulted in a large set of H1700 and H1600 values. In Fig. 8, the H1600 values are plotted with respect to the H1700 values. Some remarkable observations can be made. First, it is seen that there exists a good linear relationship between H1600 and H1700 values. This is clearly the case for the samples that were heated or irradiated in the presence of oxygen (including the radioactive samples). It is possibly also the case for the samples irradiated in absence of oxygen, but in this case more data for higher absorbed doses are needed to ascertain this (linear regression with the available data yields a regression line that is very similar to the regression line for the heated samples, whereas the data in Fig. 8 suggest a steeper slope).

The linear relationship suggests that the formation of carbon carbon double bonds is favoured in the presence of oxygen, i.e. when at the same time C=O functional groups are produced. When no or little oxygen is available, carbon carbon double bonds are formed with much less C=O functional groups being formed (with possibly a much steeper slope of the regression line). Second, the slope of the curves differ according to the treatment. The smallest

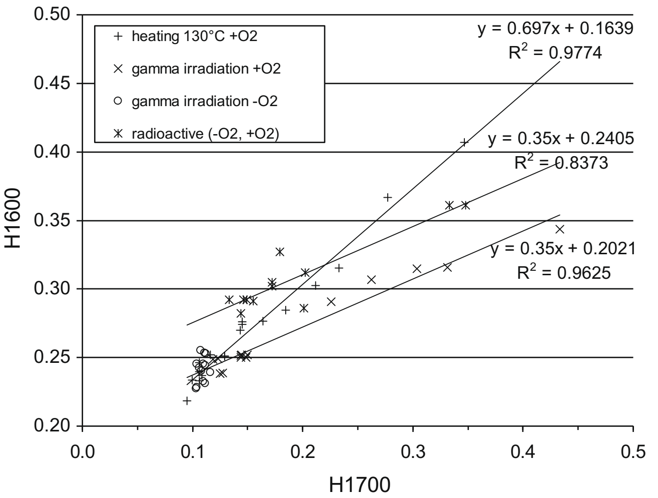

Fig. 8. Relation between H1600 (C=C) and H1700 (C=O) values for non-radioactive and radioactive Eurobitum samples that were aged by heating or irradiation, in the presence or absence of oxygen.

slope is observed for the samples that were alpha–beta–gamma-irradiated (radioactive Eurobitum) or gamma-irradiated (non-radioactive Eurobitum) in the presence of oxygen. The slopes for these two treatments are remarkably similar, but for a given H1700 value the respective H1600 value is about 0.04 units higher for the radioactive Eurobitum. This might be due to a first alpha–beta–gamma-irradiation period in the absence of oxygen (or under very low oxygen concentrations) shortly after the production of the radioactive Eurobitum. In this initial stage, the bitumen surface was not yet heavily oxidised, and no or very little fissures were present in the material, thus limiting the oxygen intrusion in the waste. During this 'anaerobic' period, mainly the number of carbon carbon double bonds increased (cfr. Fig. 8, tendency for the samples that were gamma-irradiated in absence of oxygen (○). But the difference can also be due to the different nature of the irradiation: gamma irradiation for non-radioactive Eurobitum, versus alpha–beta–gamma irradiation for radioactive Eurobitum. For the heated non-radioactive Eurobitum, the slope is two times higher than for the irradiated systems. Thus, for a given amount of C=O functional groups formed, relatively more carbon carbon double bonds are formed when the sample is heated instead of gamma-irradiated. This means, a.o., that heating of non-radioactive Eurobitum as a way to produce samples with characteristics of aged Eurobitum, does not allow to produce a fully 'representative' aged sample (in terms of number of C=O and C=C groups). It is unclear whether these differences in C=O/C=C ratio will have a large effect on the water uptake and $NaNO_3$ leaching properties of the aged Eurobitum. Possibly, gamma irradiation of non-radioactive Eurobitum (with a sufficiently high $NaNO_3$ content) at high temperature, to release oxygen generated by irradiation of $NaNO_3$, is an interesting option. However, it is not clear whether these differences in H1600 (C=C) to H1700 (C=O) ratio for heated and irradiated samples will have an effect on the water uptake, swelling, and pressure increase processes of Eurobitum in underground disposal conditions.

5. Conclusions

The rheological properties of bitumen and of bituminised waste evolve with time, a process which is called ageing. Strongly aged bitumen is harder and more brittle, full of microfissures, and has decreased adhesive properties. These changed properties may affect the processes of concern for the geological disposal of this waste, in particular water uptake, swelling and pressure increase, and $NaNO_3$ leaching. Oxidation of bitumen is the most important chemical ageing process, especially when the bitumen is heated and/or irradiated in the presence of oxygen. Oxidation leads a.o. to an increased number of C=O and C=C groups. This goes along with an increased asphaltene content, and hence an increased affinity for water.

In the work reported here, we studied the degree of oxidation of reference radioactive and non-radioactive Eurobitum and Mexphalt R85/40, as well of non-radioactive Eurobitum that was heated or gamma-irradiated in the presence or absence of oxygen. Attenuated Total Reflectance – Fourier Transformed InfraRed spectroscopy (ATR-FTIR) is a very convenient technique to study the increase of the number of C=O and C=C groups. We opted for evaluating the peak height of the IR stretching bands of these functionalities (peak maximum at respectively 1700 cm^{-1} and 1600 cm^{-1}) to compare the degree of oxidation for the different samples.

Both heating and internal (radioactive Eurobitum) and external (non-radioactive Eurobitum) irradiation increase the number of C=O and C=C groups, and a concomitant hardening of the sample (decreased needle penetration depth and increased ring and ball softening point). The increase of the number of C=C groups seems to be linearly related to that of C=O functional groups, and is much higher when the ageing treatment occurs in the presence of oxygen. It therefore appears that the generation of C=O groups promotes the production of C=C groups. The curves of the C=C–C=O relationship are remarkably similar for the gamma-irradiated non-radioactive Eurobitum and the alpha–beta–gamma-irradiated radioactive Eurobitum (slope for both curves = 0.35). The fact that the regression line for the radioactive Eurobitum has a higher intercept is probably due to an initial period of irradiation in absence of oxygen. The amount of C=C double bonds increases faster with increasing number of C=O groups when the bitumen is heated (slope 0.70), compared to gamma irradiation or internal radiation. Heating therefore proves to be more efficient in oxidising the Eurobitum than irradiation, but the C=O/C=C ratio in aged Eurobitum that was heated is different from material that was irradiated. For both ageing treatments, the availability of oxygen is a limiting factor, and unless the sample is continuously mixed (which is only possible for heated samples), a strong oxidation is only observed at the surface of the samples. For Eurobitum samples that were gamma-irradiated at dose rates of 20–140 Gy/h, the oxidation becomes small to negligible at a depth of only 3–5 mm, due to the low oxygen concentration (diffusion limitation). Only below 45 Gy/h, the dose rate becomes the limiting factor; above this threshold, the availability of oxygen becomes the limiting factor (at a depth of 3–5 mm).

When gamma-irradiated in absence of oxygen, we observe only a slight increase of the number of C=C double bonds, with almost no increase of C=O. There was probably a small reaction with oxygen that was still adsorbed on the bitumen, during the ageing treatment and during the preparation of the sample for ATR-FTIR analysis. It is not clear whether this increase of C=C bonds without increase of the C=O bonds has a strong effect on the relative amounts of the four classes of bitumen: double bonds can be formed at some places but meanwhile disappear at other places. This observation shows that gamma irradiation of $NaNO_3$ at ambient temperature does not result in the production of oxygen that is available for reaction with the bitumen. According to literature data, heating or dissolution of the gamma-irradiated $Na(NO_3,NO_2)$ crystal is necessary to release the radiolytically produced oxygen.

The results of this study thus allow to making the following conclusions:

(i) Radioactive Eurobitum will age harder starting from the surface. Oxidation further away from the surface mainly occurs through diffusion of oxygen. At the relatively low dose rates prevailing inside the bituminised waste ($< \sim 5$ Gy/h), a relatively large fraction of the oxygen that diffuses into the waste remains available for diffusion deeper into the waste. In addition, the strong fissuring caused by the extreme ageing of the surface layer favours the diffusion of oxygen deeper in the waste. As a consequence, a noticeable oxidation (increase of number of $C{=}O$ and $C{=}C$ functionalities) up to a depth of $\sim$25 cm could be observed. We can therefore expect that with time an important part of the Eurobitum will be strongly oxidised, with changed properties towards uptake of water, swelling, swelling pressure build-up, and leaching of $NaNO_3$. The thickness of the oxidised layer depends on the time between production and underground disposal. In the absence of oxygen, there is a small increase of the number of $C{=}C$ double bonds with the number of $C{=}O$ groups remaining nearly constant. At first sight, it appears that the properties of radioactive bituminised waste that aged in absence of oxygen did not change very much. Water uptake experiments with more and less oxidised radioactive samples are now underway.

(ii) To produce artificially aged non-radioactive Eurobitum samples for water uptake and swelling studies, a combination of heating (under constant mixing to maximise the contact with oxygen) and gamma irradiation in the presence of oxygen, is the best option. However, this becomes a challenge when larger amounts of bitumen are to be prepared, due to difficult handling of the material with increasing treatment time (increased hardening). In addition, irradiation in the presence of oxygen only oxidises the upper surface layer. To obtain bituminised waste samples of e.g. 10 mm thick (such as the samples used for water uptake tests) with a constant degree of oxidation throughout the thickness of the sample, gamma irradiation at a high temperature – sufficiently high to release the oxygen that is produced from the gamma irradiation of $NaNO_3$ – might give better results, at least if the needed temperature is not too high (the temperature during the irradiation is limited by the capacity of irradiation facility, the risk of melting and, at higher temperature, self-ignition of the Eurobitum).

It has to be noted that the observations and conclusions reported in this study were made for bituminised waste containing oxidised (hard, blown) bitumen Mexphalt R85/40, and are not necessarily valid for bituminised waste made with distilled (soft) bitumen, such as the French (COGEMA-AREVA) bituminised waste. It is likely that in soft bitumen the polar groups are well peptised, which makes them almost inaccessible for oxygen ('SOL' type bitumen). Oxidation of the highly reactive asphaltenes and resins is difficult, and the newly formed polar groups are also quickly 'dispersed' in the bitumen. In hard, blown bitumen, the polar groups have rather formed a continuous network with a large surface area, which makes them more easily accessible for oxygen and further mutual reaction ('GEL' type bitumen).

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