

Background

Since the end of the 1970s, about 3000 m³ of Eurobitum bituminised radioactive waste has been produced by the EUROCHEMIC/BELGOPROCESS reprocessing facility for the incorporation of precipitation sludges and evaporator concentrates originating from the chemical reprocessing of spent nuclear fuel. Eurobitum is a homogeneous mixture of ~60 weight% (wt%) of bitumen and 40 wt% of waste, of which NaNO₃ is the most important component (60-75 wt%). The preferred option of ONDRAF/NIRAS for the long-term management of Eurobitum is final disposal in a geologically stable underground clay formation. The Boom Clay is presently being studied as a reference host formation. Due to a combination of favourable properties, the Boom Clay will 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, the processes induced by the emplacement of Eurobitum should not negatively affect the long-term safety functions of this barrier. Basically, two types of disturbances can be distinguished:

1. a mechanical disturbance, caused by the build-up of a pressure in and around the waste, (a) due to the uptake of water by the dehydrated 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 by the release of large amounts of (a) NaNO₃ and (b) of water-soluble, organic, potentially complexing molecules due to 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, especially in the presence of oxygen and/or radiation. This ageing results in a harder bitumen, which tends to lose its binding capacity and which becomes increasingly brittle. Fissures and changes in membrane properties of bitumen in terms of oxygen and water diffusion are expected to favour the penetration of oxygen, thus amplifying the ageing deeper inside the product, and the infiltration of pore water, thus possibly affecting the swelling and the leaching of NaNO₃ and radionuclides.

Objectives

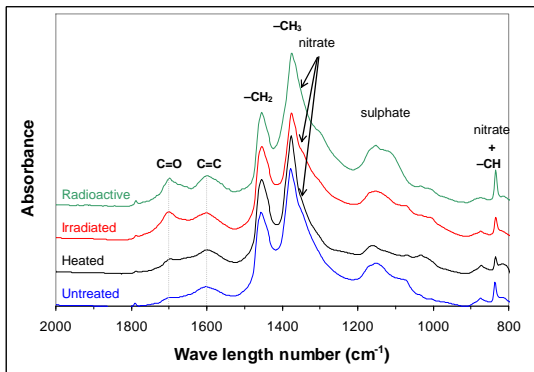
The objective of this work is to obtain a semi-quantitative understanding of the ageing of Eurobitum radioactive waste, to be able (i) to estimate the degree of ageing at the time Eurobitum will come in contact with ground water, and (ii) to produce, by accelerated ageing techniques, non-radioactive Eurobitum samples that can be used in the studies on water uptake, swelling, and salt leaching.

Principal results

Because also radioactive Eurobitum samples were to be analysed, we opted for a characterisation technique that minimises radiation exposure, contamination risks, and secondary waste production. *Attenuated total reflectance Fourier Transform Infrared spectroscopy* (ATR/FTIR) meets very well these criteria. FTIR in the mid-infrared domain (4,000-400 cm⁻¹) allows to follow the oxidation of bitumen by measuring the increase of the height of the C=O and C=C absorption bands. ATR/FTIR requires almost no sample preparation as infrared spectra of the first few microns of the material are obtained after pressing a thin sample (10x70x3 mm³) against a pre-heated internal reflection crystal made of ZnSe (figure below). After a normalisation procedure, the height of the peaks at 1700 cm⁻¹ (C=O) and 1600 cm⁻¹ (C=C), referred to as H1700 and H1600 respectively, can be compared for different treatments. Apart from the height of the C=O and C=C peaks, the normalised FTIR spectra of the radioactive samples were similar to those of the non-treated, heated, and irradiated sample (first figure on the next page).

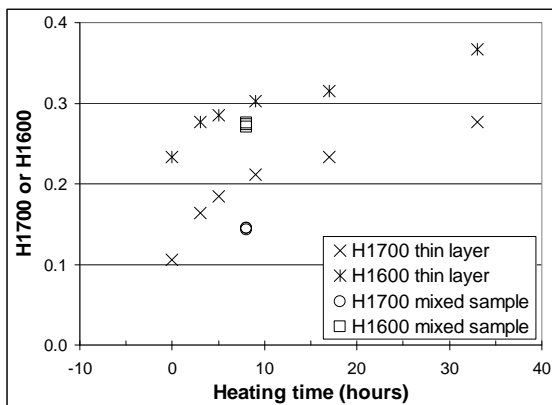
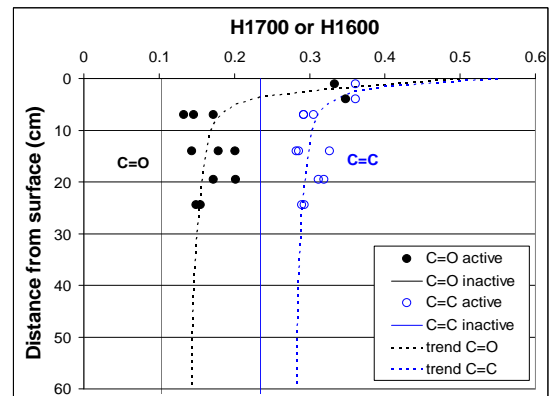


Principle of ATR/FTIR. A small bitumen sample (10x70x3 mm³) is pressed on a pre-heated internal reflection ZnSe or Ge crystal, which is then placed in the IR spectrometer. The incident IR beam is partly absorbed and partly reflected by the sample. The remaining IR light is finally re-directed towards the detector.



ATR/FTIR spectra of Eurobitum. An untreated sample is compared with a sample heated in air at 130°C for 2 hours, with one having absorbed a dose of 0.7 MGy of gamma radiation in air, and with one sampled from the upper layer of radioactive Eurobitum that was produced in 1981. Sulfates (~5 wt%) are responsible for the large band centered at 1145 cm⁻¹. Nitrates (~28 wt% in all samples) have bands at 1380-1350 cm⁻¹ (broad) and 835 cm⁻¹ (narrow). The oxidation of bitumen results in an increase of the absorbance at 1700 cm⁻¹ (C=O) and 1600 cm⁻¹ (C=C). Apart of this difference, the normalised FTIR spectra are similar for all four samples.

The figure on the right shows the height of the peaks at 1700 cm⁻¹ (C=O) and 1600 cm⁻¹ (C=C), referred to as H1700 and H1600 respectively, as a function of distance from the surface, for samples that were taken from a drum of radioactive Eurobitum that was produced in 1981. It is seen that the surface of the Eurobitum is very heavily oxidised. The material from that layer was very brittle and could be easily fragmented in small, hard particles. The degree of oxidation decreases strongly with depth, but remains higher than for a reference non-radioactive Eurobitum that was produced in 1977. The self-irradiation of the Eurobitum thus contributes noticeably to the oxidation inside the waste.



The figure on the left summarises the results of samples of a reference non-radioactive Eurobitum, produced in 1977, that were heated. Exposing thin layers of Eurobitum to air at a temperature of 130 °C results in a steady increase of the H1700 (C=O) and H1600 (C=C) values of the exposed surface. The shape of the curves shows that first the more reactive and easily accessible molecules are oxidised, and that the less reactive and less easily reached molecules react more slowly. When larger volumes of material are involved, for instance for water uptake and leach tests, the material needs to be continuously mixed to maximise the exposure of all molecules to oxygen. However, despite continuous mixing during 8 hours at ~180 °C, the H1700 (C=O) and

H1600 (C=C) values of several sub-samples were the same as the respective values for a thin layer of which the surface was exposed to air during only ~2 hours. Since after 8 hours it became difficult to further mix the sample, we conclude that heating alone does not allow ageing Eurobitum to a degree that is expected to occur when it comes in contact with water in an underground repository.

Future work

We need to better understand the kinetics of the oxidation in the bulk of the Eurobitum, and, more importantly, the consequences of the ageing for the uptake of water and the resulting swelling or swelling pressure build-up, and leaching of salts and radionuclides.

Main contact person

Elie Valcke, elie.valcke@sckcen.be

Main references

- 1) F. Rorif, E. Valcke, P. Boven, H. Ooms, J. Peeters, and S. Smets, 'Ageing of Eurobitum bituminised radioactive waste under gamma irradiation', Mat. Res. Soc. Symp. Proc. Vol. 932, 2006, p. 689 – 696.
- 2) E. Valcke, F. Rorif, and S. Smets, 'Ageing of Eurobitum bituminised radioactive waste', to be submitted to J. Nucl. Mat.

Acknowledgements

This work is undertaken in close co-operation with, and also with the financial support of ONDRAF/NIRAS, the Belgian agency for the management of radioactive waste and fissile materials. We gratefully acknowledge the assistance of BELGOPROCESS during the sampling of radioactive Eurobitum.