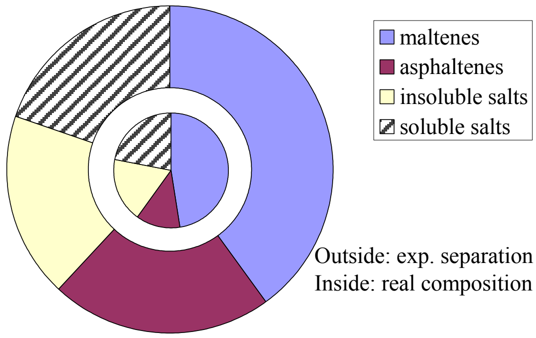
NEUTRON ACTIVATION ANALYSIS OF MALTENES RECOVERED FROM EUROBITUM SIMULATES

Background

According to the present Belgian reference scenario, Eurobitum bituminised radioactive waste has to be disposed off in a deep underground repository in a stable geological formation such as Boom Clay. This waste originated mainly from mixtures of nuclear fuel decladding slurries and waste concentrates from the nuclear fuel cycle. Even though safety assessment studies up till present do not show that this waste is unacceptable for deep underground disposal, a final decision about the disposal of the bituminised waste has not been taken so far, and alternative solutions are still conceivable. To support the decision-making we investigate methods to recondition this bituminised waste.

We continued studying a room temperature re-treatment method for Eurobitum. The aim of the method is the stabilisation and minimisation of final waste, and the free release of recovered materials. The method comprises the recovery of maltenes and water soluble salts. The recovery of maltenes is performed by dissolving the complete bitumen matrix with a "solvent", followed by the precipitation of the asphaltenes by addition of a so-called "nonsolvent". The "solvent" is a 50% aromatic blend of Shellsol A150 and Shellsol H, whereas the "nonsolvent" is aliphatic Shellsol T. The recovered maltenes represent 40 % wt of the waste, as shown in the inner pie chart. Part of the maltenes could not be recovered and remain in the asphaltene matrix, as can be seen from the difference between the inner and outer pie chart, representing the real composition and the weight fractions after separation, respectively. A second step of the room temperature re-treatment method covers the complete removal of the water soluble (nitrate) salts, and is described in the main reference and references therein.



General composition of a simulate of Eurobitum: experimental separation via room temperature retreatment versus real composition

Application of the room temperature re-treatment method results in a final waste that consists of water insoluble salts embedded in an asphaltene matrix which is less sensitive towards radiolysis than the bitumen. Moreover, the removal of maltenes and soluble salts results in an important volume reduction of the primary waste. The room temperature method is quite safe, as liquids with high flash points are used, and because volatilisation of radionuclides is avoided.

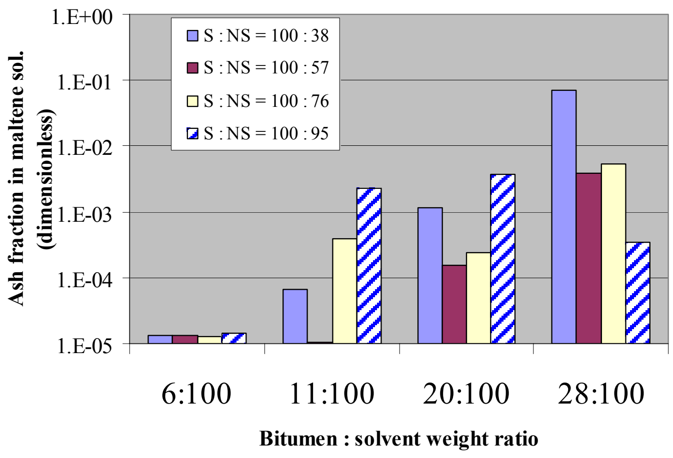
Objectives

The aim is to study the elemental composition of the non-aqueous secondary waste streams of the room temperature re-treatment method for Eurobitum. It is necessary to assess the purity of maltene solutions recovered from Eurobitum simulates in order to define experimental conditions leading to the free release of the recovered maltene solutions. As the detection limit should be very low and as we only used self-made non-radioactive Eurobitum simulates, NAA is the most suitable technique for this study.

Principal results

The complete waste matrix of Eurobitum can be dissolved in a solvent which is sufficiently aromatic. Decreasing the aromaticity by adding some nonsolvent results into the settling of the asphaltenes. The obtained solid contains the waste salts and the asphaltenes. The clarified zone containing the maltenes could be used as an organic fuel for e.g. waste incinerators, if the radionuclide content is low enough. The total amount of impurities in the clarified zone can be measured by ash analysis or NAA if the detection limit of the ash analysis is inadequate. To combine the results of the ash and NAA analyses, NAA results have to be converted into the corresponding amount of oxides as if the recovered maltene solution would be incinerated. The figure shows the ash content of recovered maltene solutions of a set of experiments as a function of bitumen – solvent (B:S) and solvent – nonsolvent (S:NS) weight ratios. The ash content of the maltene solutions of experiments with B:S equal to 6:100 is almost one order of magnitude lower than any of the other experiments. In addition, the amount of impurities in these experiments is not affected by the S:NS ratio.

The low ash quantities suggest that the maltene recovery is very promising. The results invite us to study the concentration of the radiotoxic waste elements in the recovered maltene solutions. The NAA analyses of pure bitumen type R85/25, solvent, nonsolvent (blanks) and the best recovered maltene solutions (samples) are presented in the table. Only elements which are also present in the simulated waste salt mixture are presented in the table, as only these elements are relevant for assessing the use of the room temperature re-treatment method to recover the maltenes. A lot of the waste salt elements are below the detection limit in the recovered maltene solutions even for NAA. For example Ce, which imitates the chemical behaviour of Pu present in the real Eurobitum waste is below the detection limit. However, Na, Co, Cs and Sb are detectable with NAA. The Na present in the maltene solutions is anyway not radioactive. This is not the case for Co: some ^{60}Co is present in the real Eurobitum waste. Therefore it is important to distinguish between the active Co from the waste and the inactive Co present in both the waste and the blanks. The amount of radioactive Cs and Sb in the recovered maltene solutions should also be assessed. Therefore, repeating the best experiments using real radioactive Eurobitum waste is necessary.



Ash fraction of recovered maltene solutions as a function of bitumen – solvent and solvent – nonsolvent ratio.

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Elements	Nonsolvent	Solvent	R85/25	1	2	3	4
Na (µg/g)	/	/	14.77	0.5	0.5	0.4	0.4
Co (µg/g)	0.011	0.009	0.300	0.062	0.055	0.041	0.04
Cs (µg/g)	/	/	/	0.010	0.008	<0.01	0.01
Sb (µg/g)	/	/	/	0.007	0.007	0.006	0.006
Ru (ng/g)	/	/	/	<40	<40	<40	<40
Fe (mg/g)	/	/	/	<4	<5	<5	<6
Zr (mg/g)	/	/	/	<3	<4	<4	<4
Ba (mg/g)	/	/	/	<1.5	<1.5	<2	<3
Cr (ng/g)	/	/	/	<60	<70	<70	<80
Ce (ng/g)	/	/	/	<40	<40	<50	<50
Pt (ng/g)	/	/	/	<60	<150	<100	<150
Sr (µg/g)	/	/	/	<4	<4	<3	<4

NAA of blanks and recovered maltene solutions from Eurobitum simulates. Slashes indicate that the values are below the detection limit. For experiments 1-4, the value of the detection limit is given as a guideline. As can be seen, the detection limits slightly depend on the complete composition of the samples.

Future work

The purity of the recovered maltene solutions suggests further testing of the room temperature re-treatment method using real radioactive Eurobitum waste. In this way we can study the free release of both the aqueous and non aqueous secondary waste streams of this method. At the moment, we are testing the recovery of solvent and nonsolvent from the maltene solutions. Leach tests to assess the stability of the final waste containing the asphaltenes and water insoluble salts are planned for the near future.

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Main reference

N. Impens, M. Bruggeman, S. Dekelver, P. Vermaercke, J. Van Laer, A. Fonteyne, L. Sneyers, "*Assessment of the Recovery of Maltenes from Bituminised Waste Simulates*", Proceedings of The 6th International Conference on Petroleum Phase Behaviour and Fouling, Amsterdam, The Netherlands, June 2005.