



HAL
open science

Quantitative and qualitative analysis of hydrosoluble organic matter in bitumen leachates

Isabelle Walczak, Marie-Françoise Libert, Sylvie Camaro, Jean-Marie Blanchard

► **To cite this version:**

Isabelle Walczak, Marie-Françoise Libert, Sylvie Camaro, Jean-Marie Blanchard. Quantitative and qualitative analysis of hydrosoluble organic matter in bitumen leachates. *Agronomie*, 2001, 21 (3), pp.247-257. 10.1051/agro:2001121 . hal-00886113

HAL Id: hal-00886113

<https://hal.science/hal-00886113>

Submitted on 11 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Quantitative and qualitative analysis of hydrosoluble organic matter in bitumen leachates

Isabelle WALCZAK^a, Marie-Françoise LIBERT^{a*}, Sylvie CAMARO^a, Jean-Marie BLANCHARD^b

^aCEA/DCC/DESD/SEP/LCCM, C. E. Cadarache, 13108 Saint Paul-Lez-Durance, France

^bINSA LYON-LAEPISI, 69100 Villeurbanne, France

(Received 16 September 1999; revised 25 September 2000; accepted 18 January 2001)

Abstract – Bitumen is currently used as an embedding matrix for low and intermediate level radioactive waste disposal in deep sediments. High impermeability and a great resistance to most chemicals are the two main properties sought. Indeed, the generation of water-soluble organic complexing agents could affect the integrity of the wasteform due to an increase of radionuclide solubility. Therefore, the aim of this study is the quantitative and qualitative characterisation of soluble organic matter in bitumen leachates. Different conditions of leaching solutions were tested such as various pHs, ionic strengths and S/V ratios, in order to simulate the expected deep environment of bitumen waste disposal. In water, at neutral pH, the amount of soluble organic matter released is very low. However, the amount of soluble total organic carbon released increased with pH. Nonetheless, in alkaline solutions (pH 13.5), the effect of the ionic strength leads to a decrease of soluble organic matter released. Several classes of organic compounds such as naphthalene, alcohols, linear carboxylic acids, aromatics, glycols, and nitrogen compounds were identified by GC-MS.

bitumen / leaching / organic matter / GC/MS analysis / chemical degradation

Résumé – Détermination qualitative et quantitative de la matière organique issue de la lixiviation du bitume. Le bitume, matériau organique relativement imperméable et inerte face à la plupart des agents chimiques, est un des matériaux d'enrobage des déchets nucléaires de faible et moyenne activité. L'objectif de ce travail est de caractériser de façon qualitative et quantitative les composés organiques que le bitume peut relâcher en présence d'eau dans différentes conditions de pH et de force ionique, conditions simulant l'environnement supposé des déchets bitumés. Ces composés peuvent complexer les radioéléments et par conséquent augmenter leur solubilité et diminuer le pouvoir de confinement du bitume. L'augmentation de pH induit une augmentation de relâchement des composés organiques hydrosolubles. Les espèces mises en évidence sont des composés oxydés, des composés azotés et aromatiques. L'effet de la force ionique, toujours à pH basique, tend à diminuer la concentration en carbone organique total lixivié et en composés solubles comme les acides carboxyliques.

bitume / lixiviation / matière organique / analyse par CPG/SM / dégradation chimique

1. INTRODUCTION

Bitumen is a complex mixture of aliphatic and aromatic hydrocarbons [9] of molecular weights ranging

from a few hundred to above 10^5 . It mainly consists of carbon (80–90%), hydrogen (8–11%), oxygen (0–12%), sulphur (1–7%), nitrogen (0–1.5%) and traces of metals such as nickel and vanadium [2]. The different

Communicated by Gérard Guyot (Avignon, France)

* Correspondence and reprints
marie.libert@cea.fr

hetero-atoms are included in bitumen in different structures [3, 7, 11]. Bitumen can be used to embed most wastes because of its high impermeability and its great resistance to most chemicals [2].

Unfortunately, the presence of water can modify the confinement properties of bitumen [Brodersen, unpublished data]. On the one hand, organic compounds leached from bitumen may complex heavy metals [12] and increase their solubility in the environment. On the other hand, water allows microorganisms to develop. Although the rate of biodegradable carbon from our specific bitumen is low (only 0.28% of the carbon is biodegraded in CO₂ in anaerobic conditions when all nutrients are present), soluble organic matter can be degraded by microorganisms [6].

Our aim is to qualify and quantify the organic matter present in bitumen leachates.

Previous results concerning the identification of this organic matter have essentially described the release of organic acids in pure water [10]. Here different leaching solutions were used, such as pure water, alkaline water, or water with high ionic strength, in view of the future deep environment of bitumen waste.

Extraction techniques used before gas chromatography-mass spectrometry (GC-MS) analysis seem to be convenient. Two of them, the Solid Phase Extraction (SPE) [4] and the Solid Phase Micro-Extraction (SPME) [13] include a preliminary step (where the organic substances are transferred from water to a solid phase), followed by an injection into the chromatographic device (a capillary column interfaced with a mass detector). A third analytical procedure (headspace) allows the injection of the volatile components after sample heating [8].

This study is the starting point in our effort to improve the knowledge on bitumen behaviour in the presence of water. Other tests must be performed on the behaviour of bitumen waste in its future deep environment.

2. EXPERIMENTAL CONDITIONS

2.1. Materials and experiments

In order to obtain a large bitumen surface in relation to the amount of water and short diffusion distances for hydrophilic compounds from the interior of the bitumen to the outside water-exposed bitumen surface, the bitumen is ground. Bitumen samples are first frozen at -10 °C and then immediately ground in a mortar. One gram of bitumen ground in these conditions represents a surface of about 400 cm². The surface of bitumen particles is estimated with an optical microscope. The characteristics

Table I. Characteristics of bitumen.

Penetration depth	60 1/10 mm	
Chemical composition	% C	84.5
	% H	10.2
	% O	< 0.3
	% N	0.99
	% S	4

of bitumen used in our experiments are reported in Table I. The penetration depth, determined according to NFT 66-008 represents the bitumen hardness. The bitumen used in this study is supplied by The TOTAL Company. It is the same as that used for embedding nuclear waste in the plant of La Hague-France.

Experiments have been performed in glass vials allowing gas and liquid sampling where pure 70/100 bitumen was exposed to water according to conditions described in Table II. The leaching experiments (described in Tab. II) are conducted for about two months and performed in static conditions, without water replacement. The temperature is maintained at 10 °C to avoid bitumen aggregates.

The water used in these experiments is ultrapure water obtained through a MILLIPORE filtration system, and pH 8 water is obtained with sodium hydroxide.

A high ionic strength water is obtained with a saturated solution of sodium nitrate (7.7 M). The cement-balanced solution corresponds to a reconstituted solution containing the soluble mineral elements constitutive of a CPA (Artificial Portland Cement) matrix. The TOC (Total Organic Carbon) content of these solutions was determined to be equal to 1 mg/l.

At regular intervals (see results) liquid samples were filtered (0.22 µm) and frozen to avoid the development of bacteria.

2.2. Analytical procedures

The SPME fibre coated with polyacrylate and the SPE cartridge (LC-18) were purchased from SUPELCO.

For the SPME experiments, the polyacrylate fibre was placed in 10 ml of the leaching solution. Salts (5 g of NaNO₃) were added to increase the extraction efficiency. Agitation was also used to increase the rate of adsorption. The time for adsorption was set at 20 min. Then the fibre was desorbed directly in the liner of the GC (Gas Chromatograph). Compounds such as ketones, aldehydes, alcohols, carboxylic acids and phenols were

Table II. Description of leaching solutions.

Experiment No.	1	2	3	4	5	6
Bitumen weight (g)	0.1	10	30	1	1	1
Volume (ml)	1000	1000	1000	130	1000	130
Type of water	ultrapure water	ultrapure water	ultrapure water	ultrapure water	ultrapure water	NaNO ₃ ⁻ saturated water
7	8	9	10	11	12	13
1	1	1	1	1	1	1
1000	130	1000	130	1000	130	1000
NaNO ₃ ⁻ saturated	pH 8 water	pH 8 water	cemented water	cemented solution	NaNO ₃ ⁻ saturated cemented solution	NaNO ₃ ⁻ saturated cemented solution

detected after a preliminary extraction with SPME. This technique gives a qualitative screening of the different compounds in the solution but does not allow for a direct quantitative analysis of organic products. The identification of organic substances is based on mass spectral data (data bank, match quality > 90%) and on the retention time of compounds.

Naphthalene: 129, 128, 101, 87, 75. Eicosane: 113, 99, 85, 71, 57. Heptadecane: 113, 99, 85, 71. Cyclodecane: 111, 97, 83, 69, 55. Biphenyl: 154, 57, 44, 43, 32. Tridecane: 113, 99, 85, 71.

Octanal: 57, 44, 43, 41, 32. Nonanal: 57, 56, 44, 43, 41, 32. Hexanol 2 ethyl: 57, 55, 43, 41, 32. Decanal: 57, 55, 44, 43, 41. Octadecanal: 57, 44, 43, 41, 32. Nonanol: 56, 55, 44, 43, 32. Dodecanal: idem decanal and retention time. Benzeneamine: 121, 106, 79, 77, 51, 44. Cyclopentanol: 71, 57, 44, 43, 32. Undecanol: idem dodecanol and retention time. Butanediol: 76, 75, 45, 44, 43. Dodecanol: 83, 69, 55, 43, 41. Hexadecanol: idem dodecanol and retention time. Hydroxyanisole: 180, 165, 57, 43, 41. Heptadecanol: 83, 69, 55, 44, 43. Nonadecanol: idem heptadecanol and retention time. Benzenediamine: 121, 105, 104, 94, 77.

For the SPE experiments, 50 ml of aqueous matrix (HCl was added to prevent the ionisation of analytes) were passed through the plastic cartridge. This type of cartridge allows the extraction of moderately polar analytes from aqueous samples to be made. 0.5 ml of methanol was added to elute the interesting compounds. SPE (with LC-18 cartridge) was used to detect the presence of linear carboxylic acids ($n < 13$) and to measure the concentration of low molecular weight compounds in this family ($n < 8$). Compounds were identified by the retention time of pure standards.

Glycols and phenols were identified by GC/MS after derivatisation with benzoyl chloride [5].

2.3. Instrumentation and analysis

Samples were analysed by means of a HP 5190 mass spectrometer-gas chromatograph (CPG/SM). The instrument was used either in a single mass analyser (this acquisition mode allows an increase in sensitivity but spectral information is not available) or in total scan (typically m/z between 30 and 425). 1 μ l was introduced into the split/splitless injector of the GC, kept at 220 °C and operating in splitless mode. The GC capillary column used was an HP-INNOWAX (ID = 0.25 mm, film thickness = 0.25 μ m, length = 30 m). For the SPE and SPME experiments, after injection, the oven was maintained at 40 °C for 2 min then raised to 105 °C at 40 °C/min and then raised to 250 °C at 8 °C/min.

An ASTRO total organic carbon analyser allowed the quantification of leachable compounds. It can measure TOC by ultra-violet promoted persulphate oxidation which is followed by infrared CO₂ dispersion. Inorganic carbon is removed by internal acidification and sparging. Considering the precision of the TOC-analyser, a variation of 0.4 mg/l in the TOC concentration is not significant. The aim of the TOC-analysis was to determine the kinetic of leaching and the quantity of leachable organic matter. It gave no answer as to the nature of analytes.

3. RESULTS AND DISCUSSION

3.1. Leaching in ultrapure water

Figure 1 shows total organic carbon concentration (in mg/l) for experiments No. 1, 2 and 3 (described in Tab. II) versus leaching time for three different bitumen surface/leaching solution volume ratios. In these different experiments, the TOC concentration quickly becomes constant whatever the Surface (S)/ Volume (V) ratio.

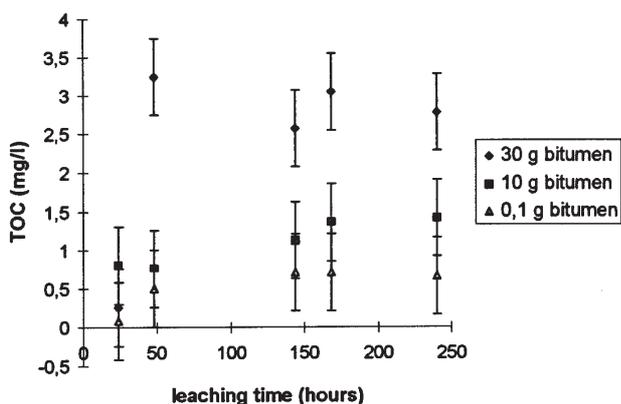


Figure 1. TOC release for different S/V ratios in ultrapure water.

No difference in the TOC concentration between a leaching time of 150 hours and 600 hours was observed. This shows that the kinetic of organic matter solubilisation in ultrapure water is very fast.

GC/MS results (chromatograms and spectra) are indicated in Figures 2, 3 and 4.

The identification of organic substances is based on mass spectral data (see Sect. 2.2).

Qualitatively, the GC/MS chromatogram after an SPME extraction (Fig. 2) shows the presence of aromatics

and alkanes in ultrapure water leachates. After the SPE extraction, carboxylic acids of low molecular weight (formic and acetic) were essentially detected (Fig. 4), but their concentrations were very low (see Tab. III). Concentrations of carboxylic acids in the different tests are given in Table III.

These tests achieved in ultrapure water underline the fact that the organic material concentration coming from bitumen leaching is very low.

The comparison between Test 4 and Test 6 (Tab. II) allows the effect of the ionic strength parameter to be studied. Figure 5 shows the total organic carbon concentration (in mg/L) versus leaching time for these two experiments.

Table III. Carboxylic acid concentration (mg/L) in the different leachates after two months of leaching.

	Concentration (mg/L)
Ultrapure water - 130 ml	0.64
Ultrapure water - 1000 ml	0.37
pH8-water - 130 ml	2.4
pH8-water - 1000 ml	2.1
Cement equilibrated solution - 130 ml	2.5
Cement equilibrated solution - 1000 ml	3
NaNO ₃ ⁻ saturated cement-balanced solution - 130 ml	1.4
NaNO ₃ ⁻ saturated cement-balanced solution - 1000 ml	2.2

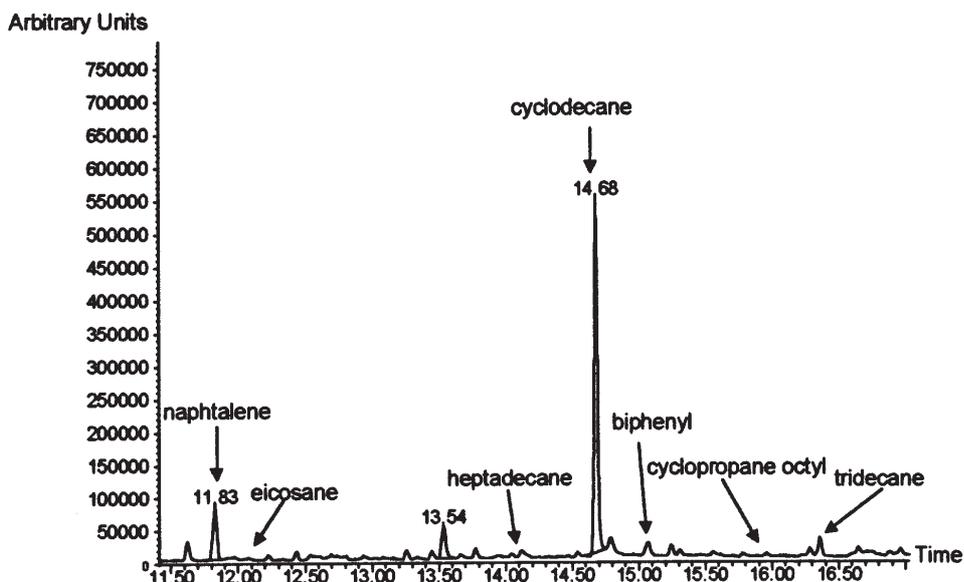


Figure 2. CPG/SM chromatogram after SPME extraction from ultrapure water.

Library Searched : C:\DATABASE\ECLT.L
 Quality : 90
 ID : docosane

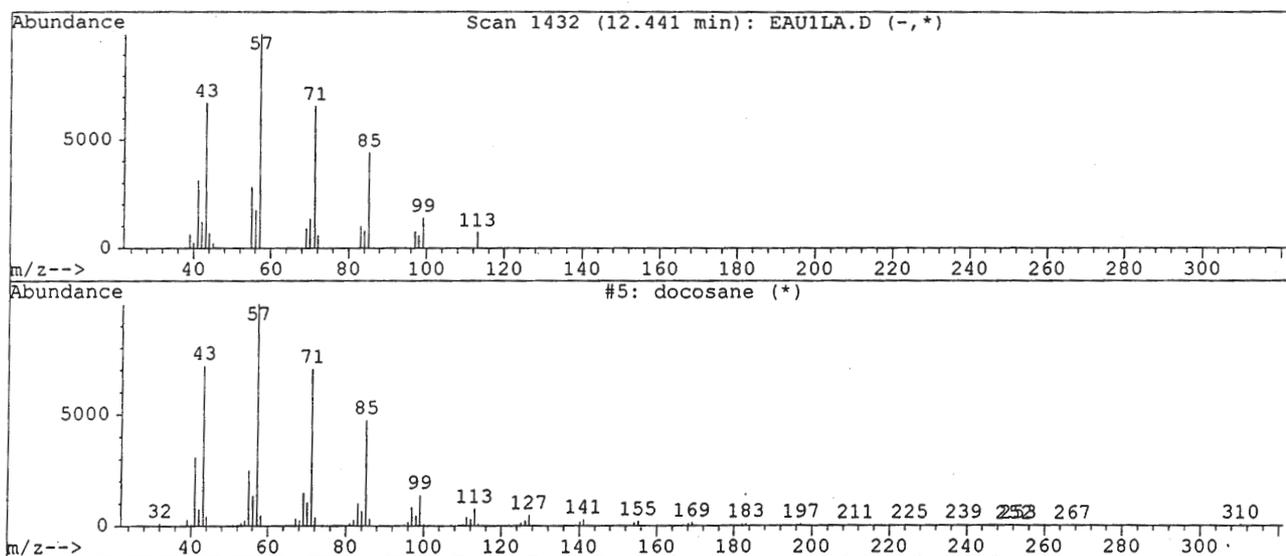


Figure 3. GC/MS spectra – Comparison of the data bank mass spectrum of docosane with the spectrum of a molecule present in bitumen leachates (SPME extraction from ultra pure water).

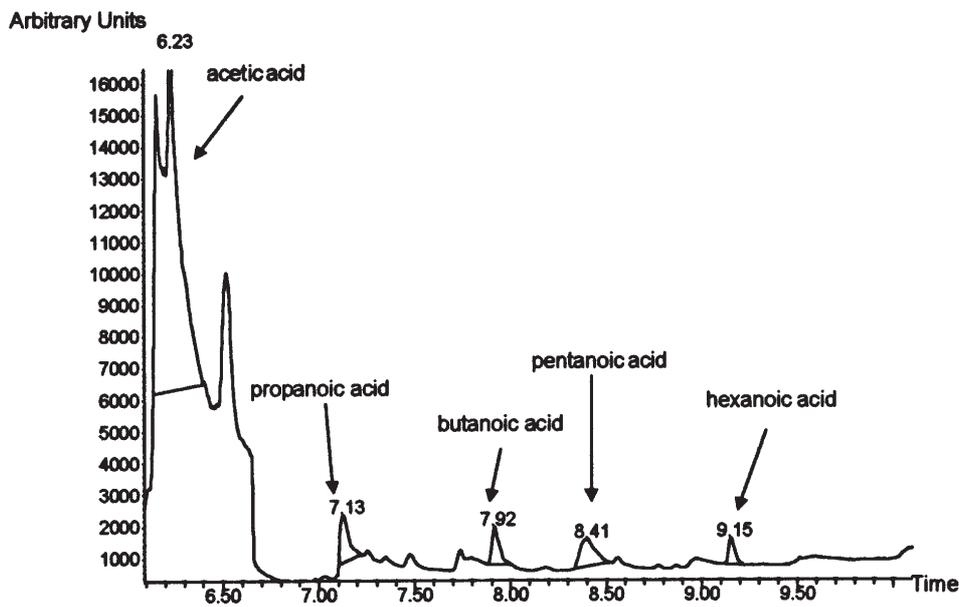


Figure 4. CPG/SM chromatogram after SPE extraction from ultrapure water.

The ionic strength influence is not significant in neutral solutions. The low TOC values obtained for both tests (consequently, errors are substantial) result in a difficulty in underscoring a difference in behaviour.

The GC/MS spectra after SPME extraction does not provide any more information on organic matter present in NaNO_3 -saturated water leachates.

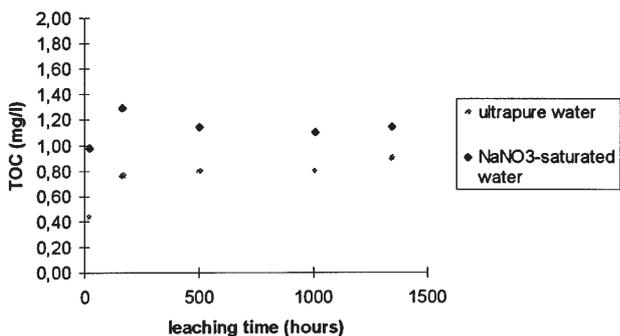


Figure 5. TOC release in water with different ionic strengths.

If the leachable organic matter is the sum of soluble organic compounds (compounds whose solubility allows their total leaching in the leachate volume in static conditions) and of slightly soluble ones (compounds whose solubility does not allow their total leaching in the leachate volume in static conditions), the proportion of each of them, in ultrapure water is (see Tab. IV):

- soluble compounds: $0.0002 \text{ mg/cm}^2 \pm 0.0001 \text{ mg/cm}^2$ of bitumen
- slightly soluble compounds: $0.7 \text{ mg/L} \pm 0.5 \text{ mg/L}$.

3.2. Leaching in alkaline water

The influence of the pH on the release of organic matter is determined thanks to experiments 8 to 13, Table II.

Figures 6 and 7 show total organic carbon concentration (in mg/L) versus leaching time for experiments conducted with alkaline water (cement-balanced solution), and for two S/V ratios.

When the pH of the leaching solutions increases, the TOC release also increases.

When the leaching solution is alkaline (pH 8 and 13.5), the release of soluble organic compounds increases with leaching time, following a logarithmic law. This

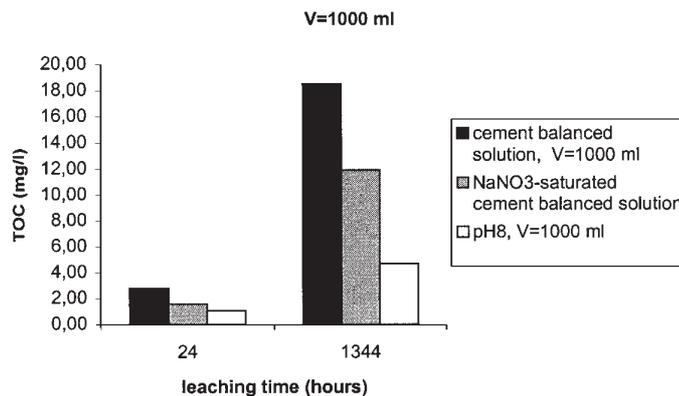


Figure 6. TOC release in alkaline solution with different ionic strengths – S/V ratio = 0.4 cm^{-1} .

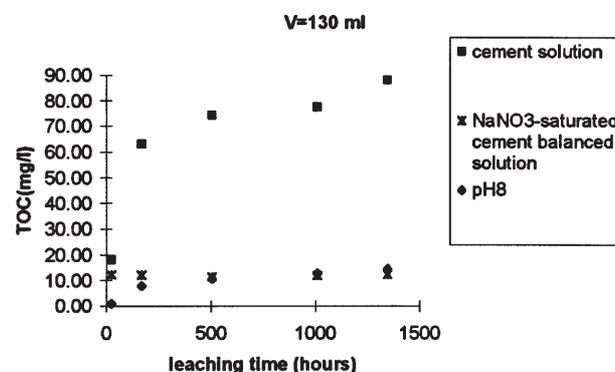


Figure 7. TOC release in alkaline solutions with different ionic strengths – S/V ratio = 3 cm^{-1} .

behaviour shows a phenomenon other than simple solubilisation: a chemical attack leading to a degradation of the bitumen (see Tab. IV).

In the pH 8 solution, carboxylic acid concentration increases with leaching time (see Tab. III). But the TOC increase is not mainly due to the increase of carboxylic acids. Other species are leached such as alcohols, linear

Table IV. Quantification of soluble and slightly soluble compounds in the different leachates after two months of leaching.

	Ultrapure water	pH8 solution	Cement-balanced water
Soluble compounds (mg/cm ² of bitumen)	0.0002	0.0035	0.026
Slightly soluble compounds (mg/L)	0.7	3	9

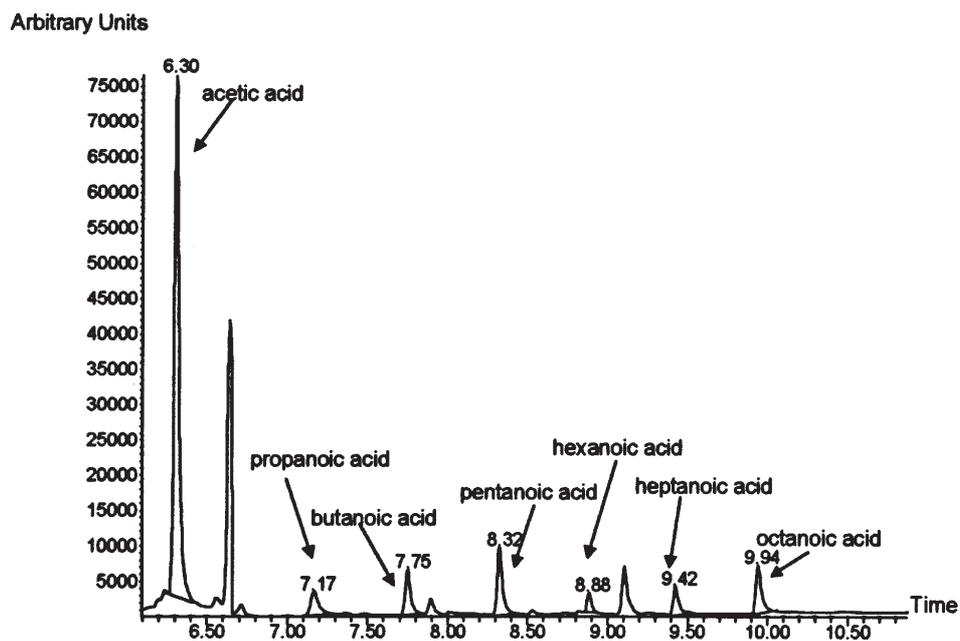


Figure 8. CPG/SM chromatogram after SPE extraction from cement-balanced solution.

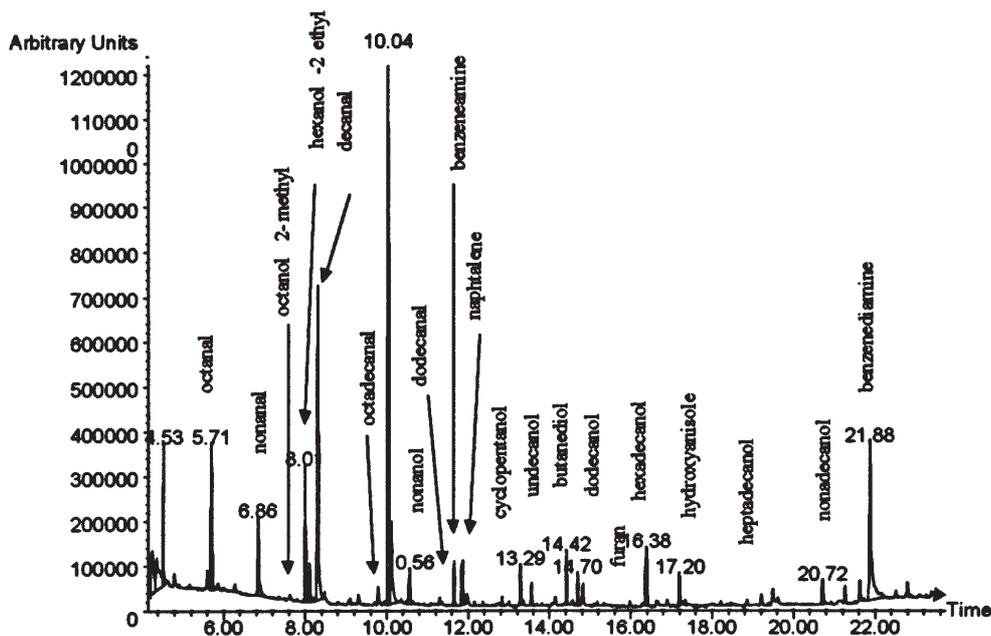


Figure 9. CPG/SM chromatogram after SPME extraction from cement-balanced solution.

carbonyls and aromatics. Neither phenols nor glycols are detected after extraction and GC/MS analysis.

In the cement-balanced solution (pH 13.5), carboxylic acid concentration is greater than the concentration obtained in the pH 8 solution or ultrapure water (see Tab. III).

GC/MS results after a SPE extraction of a cement-balanced solution) are indicated in Figure 8. Acids are essentially lower linear acids (lower than butanoic acid). The main part of the TOC is not made of carboxylic acids. The identification of organic substances is based on mass spectral data (see Sect. 2.2). Molecules

Library Searched : C:\DATABASE\NBS75K.L
Quality : 95
ID : Naphthalene

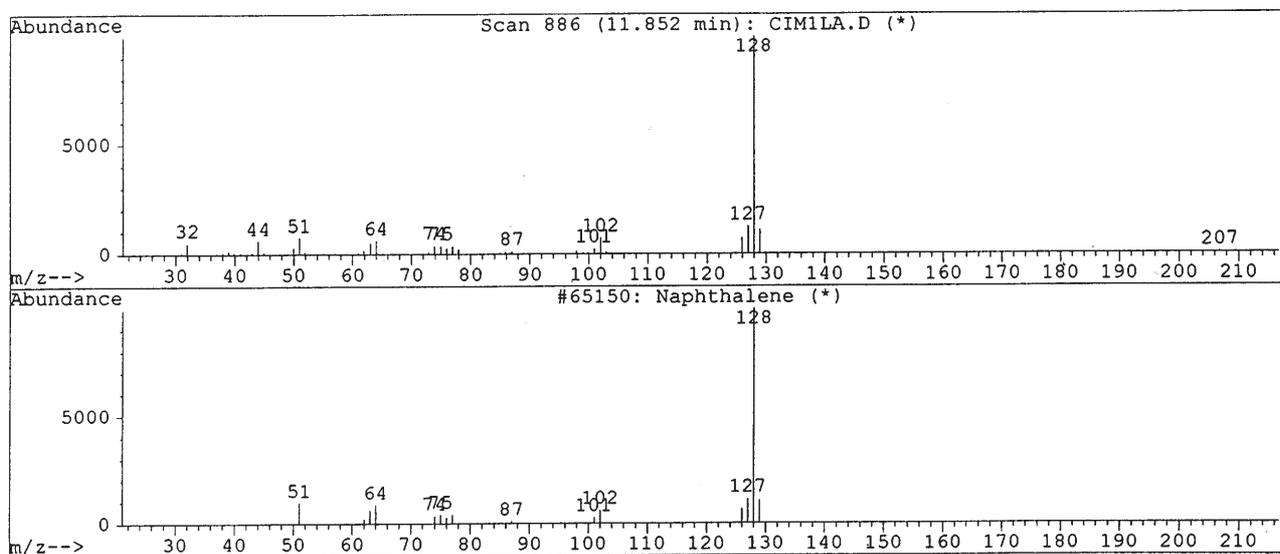


Figure 10. GC/MS spectra – Comparison of the data bank mass spectrum of naphthalene with the spectrum of a molecule present in bitumen leachates (SPME extraction from cement balanced solution).

Library Searched : C:\DATABASE\NBS75K.L
Quality : 91
ID : Nonanal

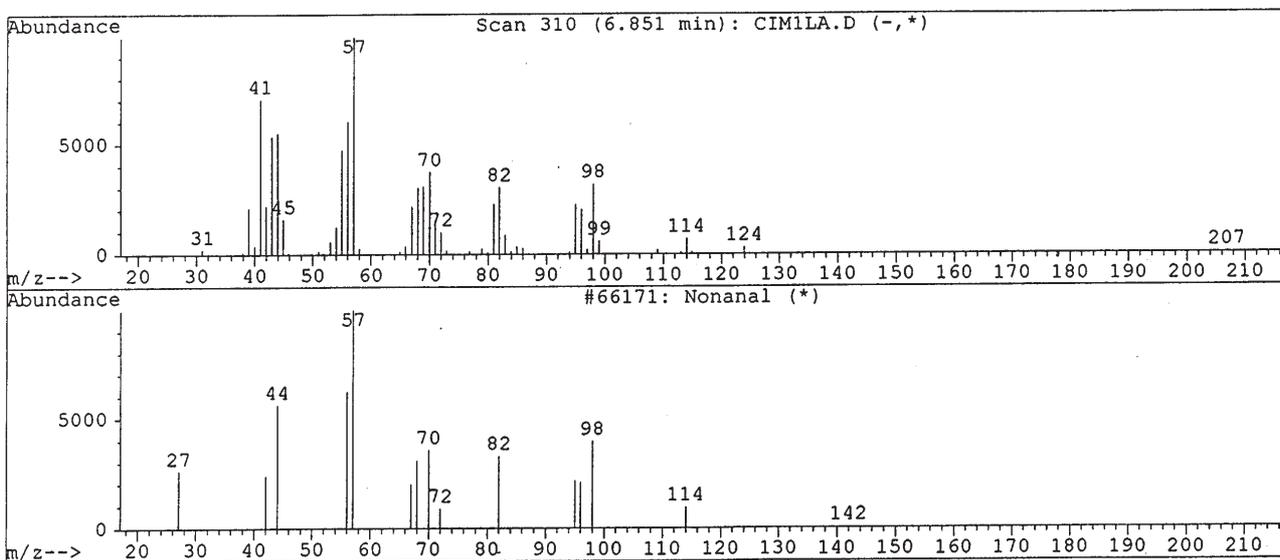


Figure 11. GC/MS spectra – Comparison of the data bank mass spectrum of nonanal with the spectrum of a molecule present in bitumen leachates (SPME extraction from cement balanced solution).

Library Searched : C:\DATABASE\NBS75K.L
 Quality : 93
 ID : 1,3-Benzenediamine, 4-methyl-

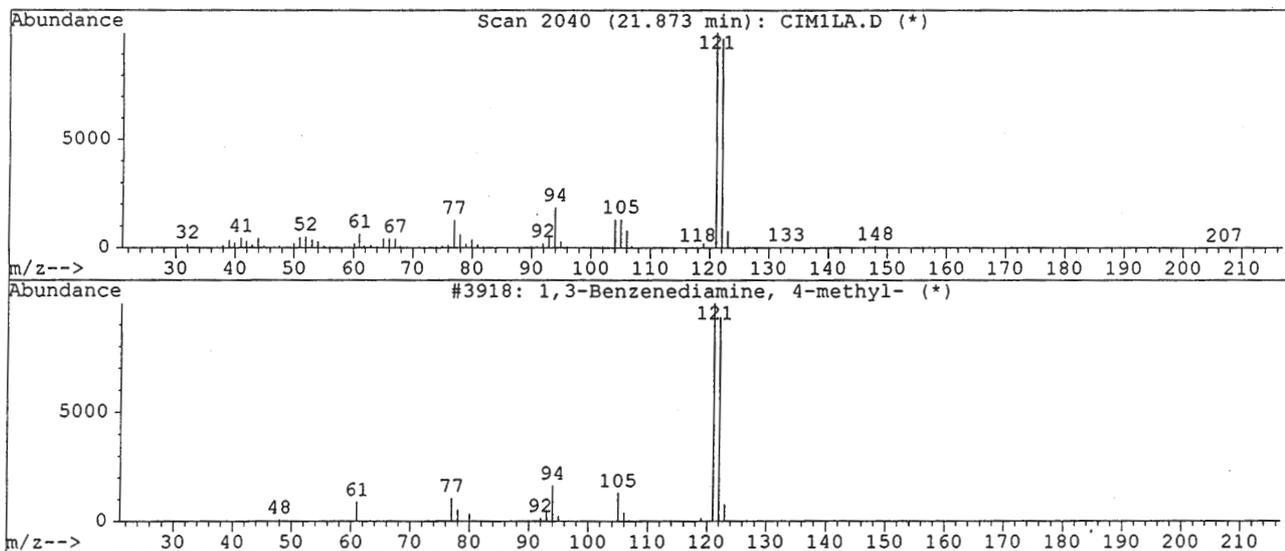


Figure 12. GC/MS spectra – Comparison of the data bank mass spectrum of benzene-diamine with the spectrum of a molecule present in bitumen leachates (SPME extraction from cement balanced solution).

Quality : 96
 ID : Cyclododecane

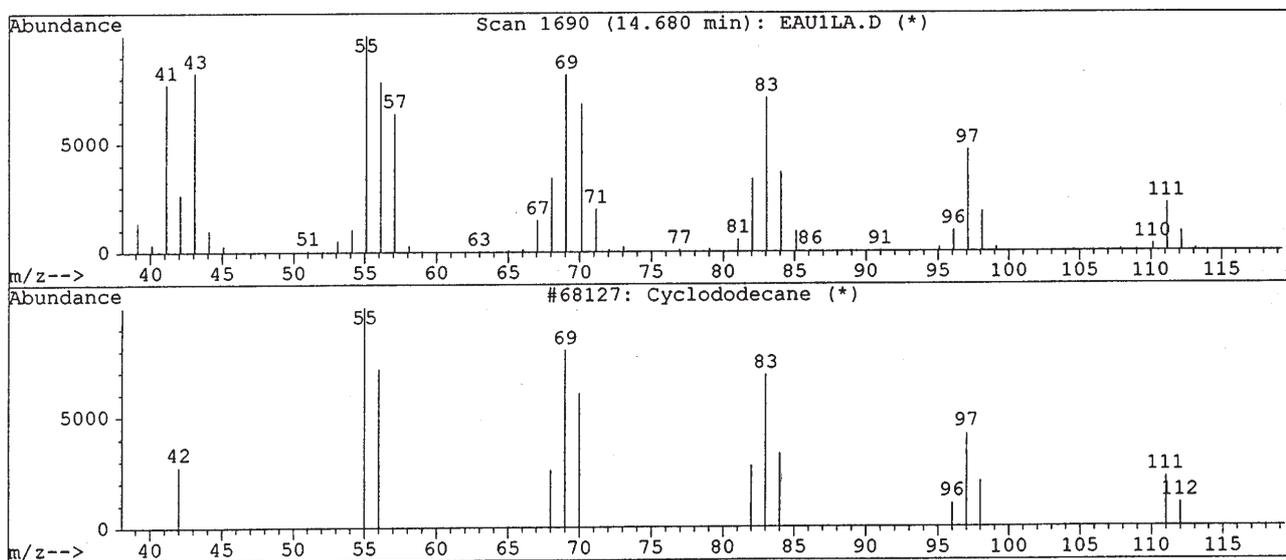


Figure 13. GC/MS spectra – Comparison of the data bank mass spectrum of cyclododecane with the spectrum of a molecule present in bitumen leachates (SPME extraction from cement balanced solution).

identified after SPME extraction and GC/MS analysis are aromatics, such as naphthalene, oxidised compounds such as alcohols, linear carbonyls, aromatics, glycols, and nitrogen compounds (Figs. 9–13). The leaching of bitumen does not seem to drag any sulphur compounds whereas bitumen contains a large proportion of sulphur.

For the cement-balanced solution (pH 13.5), the ionic strength (linked to a saturation with NaNO_3) influences the release of organic matter.

When the S/V ratio is 3 cm^{-1} , the increase of ionic strength leads to a decrease of the amount of organic matter. This observation is consistent with the solubility decrease of organic species in salt water. When the S/V ratio is 0.4 cm^{-1} , the release is equivalent both for the NaNO_3 saturated solution and the low ionic strength solution. In this case, the release should be a compromise between the decrease of organic compound solubility in salt water and the oxidising effect of nitrates.

The comparison between the chromatograms obtained for the saline water and the non-saturated one shows that the organic species are different in the two cases. The identified molecules in the saturated water are aromatics such as benzaldehyde, benzenamine, benzothiazole, benzophenone, alcohols and linear carbonyl compounds. Glycols and carboxylic acids are also leached but in lower concentrations. This is in good agreement with the solubility reduction of ionic organic species in saline water.

Table IV gives the results for soluble and slightly soluble compounds for the different types of leaching solutions.

The concentration of soluble and slightly soluble compound concentrations changed with the pH of the solution. This increase is particularly significant for the soluble compounds. This is consistent with the effect of chemical oxidation of bitumen by the alkaline solution which leaches polar compounds and then more soluble compounds.

4. CONCLUSIONS

The leaching of bitumen with ultrapure water releases only a few organic species. Due to the low content of soluble organic matter, the complexation phenomenon seems to be very low in these conditions. However, with alkaline solutions simulating the expected deep environment of bitumen waste, the bitumen degradation implies an increase of the released organic compounds.

In alkaline water, the increase of ionic strength leads to a decrease of the amount of organic matter. This

observation is consistent with the solubility decrease of organic species in salt water.

The identification of these compounds by GC/MS shows alcohols, carbonyl compounds, glycols, aromatic compounds, nitrogen compounds and carboxylic acids. All of these compounds may be complexing agents and may increase the solubility and reduce the sorption of radionuclides in their surroundings.

Deep repository conditions will allow the growth of microorganisms [1], that is why the biodegradation of these organic molecules is presently being tested. We already know that microorganisms consume most of the solubilised organic acids released by the bitumen matrix [6]. Other experiments are ongoing to detail the biodegradability of acids, alcohols and glycols in leaching conditions simulating the deep environment of bitumen waste.

The sorption of radionuclides on the bitumen matrix during the leaching is also under study to determine the behaviour of metals when two types of ligands are formed due to the chemical degradation of bitumen: free ligands in solution and bitumen ligands not yet leached.

5. REFERENCES

- [1] Camu H., Lion R., Berthelin J., Desjardin T., Bianchi A., Garcin J., Étude des microorganismes présents dans les couches géologiques profondes, Rapport CCE EUR 11141 FR, 1987.
- [2] Eschrich H., Properties and long term behaviour of bitumen and radioactive waste-bitumen mixtures, Svensk Kaernbraenslefoersoerjning AB, Stockholm, Swed. Avail, SKBF/KBS-TR-80-14, 1980.
- [3] Harlin M., Le bitume. Les liants hydrocarbonés. Lieu : Paris, Laboratoires des ponts et chaussées, Département Génie civil, rapport de recherche n° 83, 1990.
- [4] Ho J., Tang P., Eichelberger J., Budde W., Liquid–solid disk extraction followed by SFE and GC-Ion trap MS for the determination of trace organic pollutants in water, *J. Chromatogr. Sci.* 33 (1995) 1–7.
- [5] Holcapek M., Virelizier H., Chamot-Rooke J., Jandera P., Moulin C., Trace Determination of Glycols by HPLC with UV and Electrospray Ionization Mass Spectrometric Detections, *Anal. Chem.* 71 (1999) 2265–2293.
- [6] Libert M.F., Jacquot F., Romero M.A., Besnainou B., In vitro evaluation of microbial effects on bitumen waste form, in: Wolfram J.H. et al. (Eds.), *Microbial Degradation Processes in Radioactive Waste Repository and in Nuclear Fuel Storage Areas*, Kluwer Academic Publishers, Printed in the Netherlands, 1977, pp. 275–283.
- [7] Mitra-Kirtlay S., Mullins O., Branthaver J., Cramer S., Nitrogen chemistry of kerogens and bitumens from X-ray absorption near edge structure spectroscopy, *Energy fuels* 7 (1993) 1128–1134.

[8] Neu H.G., Ziemer W., Merz W., Ein neuartiges Derivatisierungsverfahren zur bestimmung von spuren polaren organischer Substanzen in Wasser mittels statischer Dampfraum-Gaschromatographie, *Fresenius J. Anal. Chem.* 340 (1991) 65–70.

[9] Seifert W.K., Effects of phenols on the interfacial activity of crude oil, *Anal. Chem.* 41 (1969) 562–568.

[10] Seifert W.K., Carboxylic acids in petroleum and sediments, in *Progress in the Chemistry of Organic Natural Products*, Springer, 1977, pp. 1–49.

[11] Simoneit B., Leif R., Ishiwatari R., Phenols in hydrothermal petroleum and sediment bitumen from Guaymas basin, gulf of California, *Org. Geochem.* 24 (1996) 377–388.

[12] Van Loon L.R., Kopajtic Z., The absorption of Cs^+ , Ni^{2+} et Sr^{2+} on bitumen: A mechanistic model, *PSI Bericht*, 88, 1998.

[13] Zang Z., Pawliszyn J., Headspace solid-phase microextraction, *Anal. Chem.* 65 (1993) 1843–1852.