Study of the effect of the fibre mass UP2 degradation products on radionuclide mobilisation

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SKB

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Foreword

This report presents a literature review and laboratory work of the degradation of the fibre UP2, as well as an assessment of the effects of its degradation products on Europium sorption onto cement, as an example of their effects on radionuclide migration. All laboratory work was performed by the Swedish groups (Linköping and Örebro Universities), who also performed some of the literature review. The data interpretation was performed by the Spanish team (Amphos 21).

SKB has combined the reports of these studies into this common document and has added minor editorial changes. All these changes have been accepted by the authors.

Svensk Kärnbränslehantering AB

Stockholm, September 2012.

Contents

1 Introduction

The SFR1 repository at Forsmark in Sweden is used for the final disposal of low- and intermediate-level radioactive waste (L/ILW) produced by the Swedish nuclear power programme, industry, medicine and research. The waste is produced at the operational stage of nuclear power plants. Cement based materials are used as the main near field barriers in this repository, which consists of one SILO and four vaults (1BMA, 1BTF, 2BTF and 1BLA). The vaults have different designs and are prepared to receive different type of wastes (Pereira and Sundström 2003, SKB 2001):

- The 1BMA vault has been engineered for receiving intermediate level waste, it is aimed at disposal of ion-exchange resins, scrap and trash conditioned in cement or bitumen.

- The 1BTF and 2BTF vaults have been engineered for receiving intermediate level waste. Ashes, ion-exchange resins and scrap are received at these vaults. Ion-exchange resins are de-watered and deposited in concrete containers. The other materials are deposited in steel drums or concrete containers.

- The 1BLA vault receives low-level waste, mainly metals, cellulose and organic materials packed and conditioned in ISO-containers.

- The SILO will mainly receive ion-exchange resins (98%) and the remaining 2% are scrap and trash. All of the waste is conditioned, about 80% in cement and 20% in bitumen.

A general overview of the repository is shown in Figure 1-1.

In SFR1 the main radionuclide retarding mechanism is sorption. The main barriers retaining radionuclides by sorption are concrete and grouting used in the repository. No concrete barriers are considered in the 1BLA vault, given that no backfill is intended to be put in place in this vault.

The sorption process of radionuclides onto cement matrices, the most abundant solid phases present in SFR1, have been widely studied in the literature. Several compilations of recommended K_d-values (distribution constant between radionuclide in solution and sorbed onto cement) for the radionuclides of interest onto cementitious matrices are available (Bradbury and Van Loon (1997), Nordén and Allard 1994, cited in Ochs et al. (1997), Van Loon and Glaus (1998)).
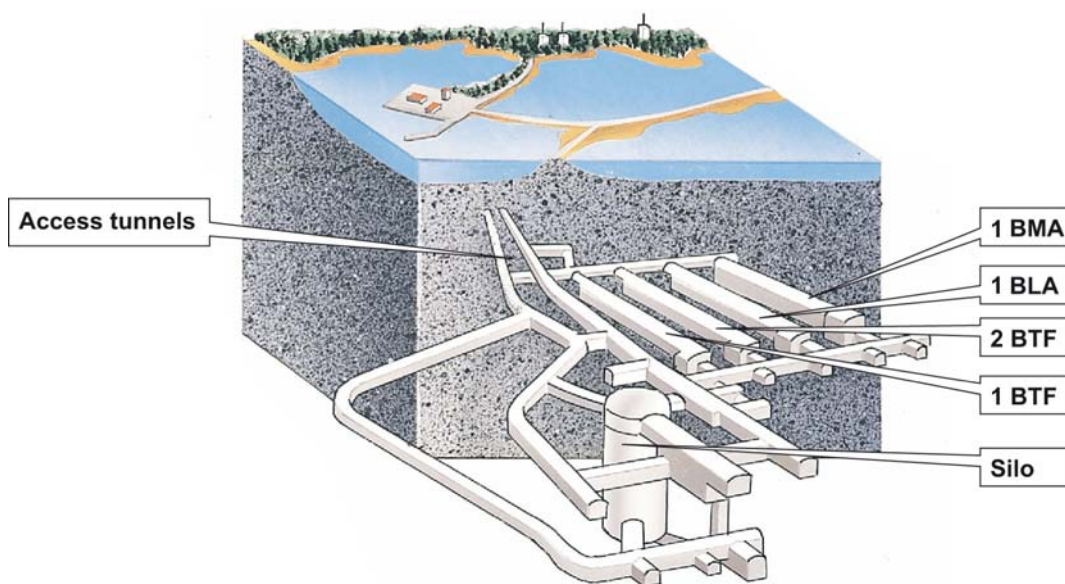

Figure 1-1. *Overview of the SFR1 repository.*

Operational waste is mainly immobilised in cement, to form a concrete waste form. The waste form might contain several organic substances, whose composition and volumes vary considerably between repositories designed for different purposes. The operational waste also contains traces of long-lived radionuclides (Albinsson et al. 1999, Dario et al. 2004a). Many of the organic substances are able to form complexes with radionuclides and this process often reduces sorption (Holgersson et al. 1998, Ledin et al. 1993) and increases the possibility of radionuclide migration. Two consequences of complex formation are of special concern within the present context:

- complexation of a metal tends to increase its solubility, and hence, its mobility;

- adsorption of metal ions may be greatly influenced by complex formation.

The effects of organic materials in SFR1 is therefore important to investigate.

UP2 is a filter aid which is used both in nuclear and in conventional power plants. The main component in UP2 is the polymer polyacrylonitrile (PAN), according to the manufacturer/supplier. The exposure of such material to slightly oxidant conditions in the nuclear power plant and its ulterior disposal in the strong alkaline conditions prevalent in SFR1 may result in a release of several organic compounds able to complex radionuclides.

So far there are only preliminary data on the effect of UP2 degradation products ,obtained at 60°C, upon sorption of cations (Dario et al. 2004a, b).

The UP2 filter aid is used at Forsmarks nuclear power plant (1FKA) in their condensate clean up ion exchange resins. These resins will be stored of in SFR1 in the 1BMA rock vault. The resins are stored of in steel moulds and stabilised in a bitumen matrix.

The assessment of the effects that UP2 may have on the release of activity from the 1BMA vault requires preliminary work to study the mechanisms and rates of degradation of UP2. This report also assesses the effect of the UP2 degradation products on the behaviour of radionuclides under the conditions prevailing in the SFR1 repository. Such degradation products can represent a health hazard by themselves, but can also modify the mobility of radionuclides present in the waste through the formation of stable aqueous complexes.

2 Literature studies on the degradation of the UP2 fibre

According to the data sheet provided by the manufacturer/supplier of UP2, its main component is the polymer polyacrylonitrile (PAN). Other components included in the filter aid are N,N-dimethylacetamide (Figure 2-1), max 0.5%, different amounts of water and finally max 3.5% of an additional component called "finish".

Polyacrylonitrile (PAN) is prepared from acrylonitrile, i.e. propenenitrile, and has the general formula $(C_3H_3N)_n$, as shown in Figure 2-2. The molecular mass of PAN in UP2 is between 100,000 and 150,000 u and the density is 1.17 g/cm^3. PAN has a softening point at 240°C. The polymer is reported to be stable in the pH-range of 2 to 12 and is insoluble in water, a prerequisite for its function as a filtering material. The polymer is stable up to 65°C.

2.1 Manufacturing of polyacrylonitrile

Polyacrylonitrile is manufactured by polymerisation of the monomer acrylonitrile. The reaction can be performed both as a radical reaction and as an ionic reaction (Figure 2-3, Campbell 1994). The ability of the intermediate to stabilise a negative charge on the carbon atom next to the nitrile group is utilised in the ionic reaction.

Independently if the polymer is synthesised by the radical reaction or the ion-reaction, the product will be a chain of the monomer acrylonitrile. Carbon atom nr 2 in the acrylonitrile molecule is always bonded to carbon atom nr 3 in the next molecule. This is due to the fact that both the intermediate anions and the radicals on carbon nr 2 are stabilised by resonance from the adjacent nitrile group (Figure 2-4).

Polymers that are synthesised by the addition of the double bond in a monomer to the double bond of the next monomer can in principle develop three different spatial structures. These are called isotactic, syndiotactic and atactic, respectively. The difference between the structures is shown in Figure 2-5.

If one imagines the carbon chain as folded, the adjacent nitrile groups can be on the same side (isotactic structure) or on different sides (syndiotactic structure) of the chain. When the configuration varies between both forms the structure is called atactic. Normally, acrylonitrile is polymerised in an atactic form.
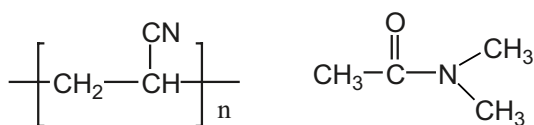

Figure 2-1. *Structural formulas for polyacrylonitrile and N,N-dimethylacetamide.*
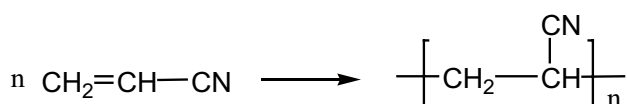
Figure 2-2. *Acrylonitrile and polyacrylonitrile.*
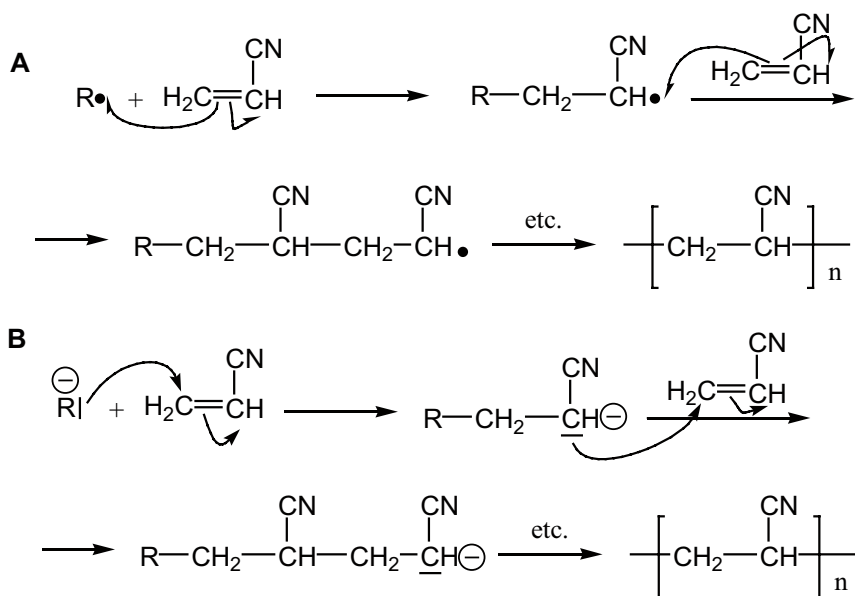
Figure 2-3. *Synthesis of polyacrylonitrile through a radical reaction (A) and an ionic reaction (B).*
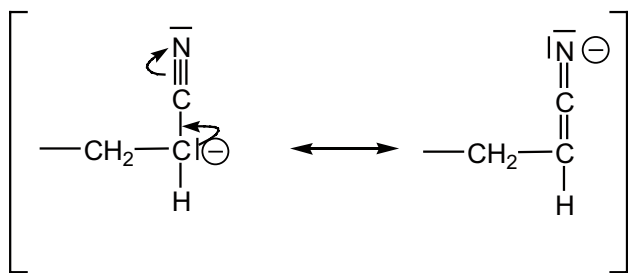
Figure 2-4. *The stabilisation of the intermediate anion.*

isotactic structure   syndiotactic structure
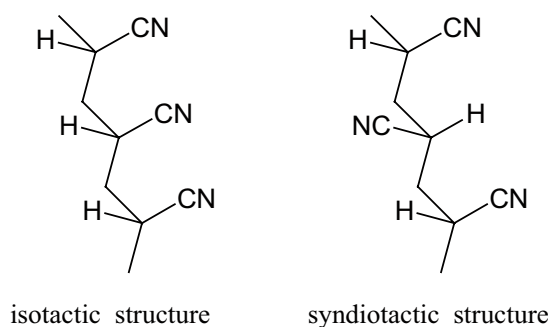
Figure 2-5. *The different configurations of polyacrylonitrile.*

2.2   Decomposition of PAN

Commercially, polyacrylonitrile is a widely used polymer, and several reports can be found on its decomposition under different conditions. Moreover, carbon fibres are manufactured from acrylonitrile through the heating of the polymer to very high temperatures. Therefore, thermal decomposition has been intensively studied. Other investigations have aimed to recycle the monomer from polymers that have been used in commercial processes. The main objective has been to get back the monomer and reuse it for synthesis of new polymers. Some studies of polyacrylonitrile have aimed to study its decomposition in the environment, both by photolysis and by microbial decomposition. In this summary, the decomposition of PAN will be discussed in the order: 1) hydrolysis, 2) thermal decomposition, 3) radiolysis, 4) microbial decomposition and 5) other decomposition studies.

2.2.1 Hydrolysis

The presence of functional groups within the polymer fibre defines special reactive sites. These sites are potential sites where degradation reactions can be activated to form further degradation products. Therefore, nitrile groups, as functional group in PAN, are sensible to suffer nucleofilic attacks on their electronically impoverished carbon atoms. In this sense, hydrolysis of PAN under alkaline conditions might be one of the several mechanisms for the fibre degradation by a nucleofilic attack.

Indeed, due to its organic character, UP2 fibre is likely to degrade when exposed to slightly oxidant media or strong alkaline media. Thus, some smaller organic compounds are possibly formed during UP2 lifetime and its ulterior disposal, facilitating the mobilisation of the radionuclides at the repository.

Some references dealing with PAN and its alkaline hydrolysis are found in the literature due to the specific applications of the hydrolysed fibre e.g. Gupta et al. (2004) or Tanaka (1982). In general terms, all the studies observed the formation of carboxylate and amide groups due to the hydrolysis of PAN. Nevertheless, there is a general lack of agreement among the different studies on which are the mechanisms responsible for the observed degradation.

During the 60's (Sadov et al. 1965, cited in Litmanovich and Platé 2000), a scheme similar to that of the hydrolysis of low molecular weight nitriles (R-C≡N) was assumed for the PAN hydrolysis, following a degradation process through amide (R-CONR$_1$R$_2$) formation and final carboxylate (RCOONa) formation.

This simple scheme was questioned two decades later by Bajaj et al. (1985), who proposed the possible PAN cyclation during its hydrolytic degradation. Although nowadays such cyclation has been confirmed, Bajaj and co-workers proposition was at that time neglected because it was not able to completely explain the observed experimental results.

The currently accepted mechanism was completed by authors from the Russian Academy of Sciences (Ermakov et al. 2000, Kudryavtsev et al. 2000, Litmanovich and Platé 2000). This mechanism confirmed the final formation of carboxylate and amide groups, via cyclation. The cyclation process is explained by the existence of amidine groups (NH=CR-NH$_2$), which act as intermediate species between the original nitrile group and the final carboxylate and amide groups (Figure 2-6).

It has been noticed for a long time that solutions of PAN become coloured if they are treated with base. Batty and Guthrie (1981) used a calculation program to identify which chromophores were formed. Earlier, the general opinion was that cyclic structures were formed according to the first three steps in Figure 2-7.

According to Batty and Guthrie (1981) these compounds are not able to show any absorbance in visible spectrum. Their calculations showed that, independently of the amount of rings and subsequently the amount of conjugated double bonds that is included in the system, the absorption λ_{max} will asymptotically go to 275 nm, which lays in the UV-region of the spectrum. The compounds could therefore not be coloured. They report that PAN during treatment with a base gives a temporary colour, which disappears when treated with an acid, and a permanent colour that is stable. Polymethacrylonitrile (PMAN) shows only the temporary colour. In principle both PAN and PMAN (Figure 2-8) can form chromophores like the substance in Figure 2-9.

The main point in Batty's and Guthrie's theory is that they claim that the conjugated system cannot be terminated with a double bond to a nitrogen atom, like the double bond in Figure 2-7 (substance 3). Instead they suggest that the coloured structures found are similar to those in Figure 2-9, in which a hydrogen atom in a tautomeric equilibrium has migrated from one carbon atom to a nitrogen atom. Their theory is supported by the fact that these kinds of structures cannot be formed from PMAN. They further claim that the coloured products are formed via a radical reaction, since the colour is not formed during oxygen-free conditions.
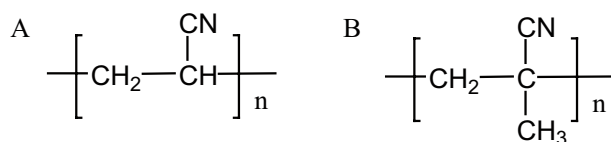
Figure 2-6. *Degradation sequence proposed by Litmanovich and Platé (2000).*

Figure 2-7. *Formation and hydrolysis of conjugated sequences (CS; from Litmanovich and Platé 2000).*

Figure 2-8. The structural formulas of (A) polyacrylonitrile and (B) polymethacrylonitrile.
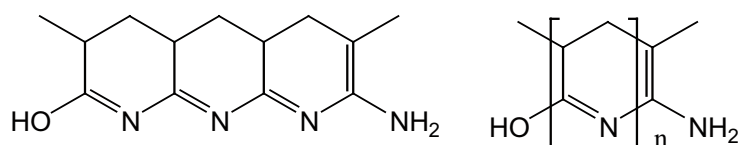

Figure 2-9. Proposed structures of the coloured compounds that are formed during the treatment of PAN with a base.

Bashir et al. (1991) studied to which extent the coloured products that were formed during treatment of PAN with a base, had cyclic structures. Their assumption was that cyclic compounds are more easily formed from isotactic than from syndiotactic structures. They used common PAN, which has an atactic structure. By using ^{13}C-NMR they could determine the relative configuration for the nearby asymmetrically substituted carbon atoms. The result showed, as expected, that the proportion of isotactic structures decreased during treatment with a base, but they could not find any structural elements with conjugated C=N groups. Instead the proportion of syndiotactic structures increased.

They made the following observations: Treatment of PAN with base gave: 1) a coloured solution, 2) initially a decrease in the viscosity of the solution, 3) after a while an increase in the viscosity of the solution, 4) the nitrile groups were hydrolysed to amides and carboxylate groups, and 5) increased proportion of the syndiotactic structure at the expense of the isotactic structures.

Their explanations were:

1. Chromophores with very high absorption formed the colour, since neither IR nor NMR could detect any conjugated double bonds.

2. First the viscosity decreased in the solution due to breakage in the chain of carbon according to the mechanism shown in Figure 2-10.

3. The increased viscosity that was observed after some time when PAN was treated with base was due to the formation of crosslinking bonds between the chains of carbon, according to Figure 2-11.

4. Hydrolysis of the nitrile groups to amides (Figure 2-12; step 1-3) and thereafter to carboxylic acids or their salts (Figure 2-12; step 4) are well known reactions. Nitriles are derivates of carboxylic acids and can react with water and acid or base to form amides and acids. Normally forced conditions are required.

5. NMR showed that the configuration of PAN changed from isotactic to syndiotactic in the presence of a strong base. According to the proposed mechanism the base attacks the proton on the carbon in the α-position forming a carbanion that is stabilised by resonance. This ion can take part in different reactions such as breaking the chain of carbon, crosslinking reactions, or in the abstraction of a proton from the solvent. Furthermore, it can undergo inversion of the configuration before another proton is added to the structure (Figure 2-13).

The degradation mechanism in Figure 2-7, proposed by Litmanovich and Platé (2000), was based on their experimental results (T=60–85ºC, NaOH/PAN=0.5 and 1.5, in ethanol/water and water) in addition of previous experimental results (Lovy and Stoy 1988, cited in Litmanovich and Platé 2000, Bajaj et al. 1985). Such mechanism leads to a broad conversion of the initial nitrile groups toward different types of hydrolysis-generated groups. According to these studies, carboxylates appear to be the main final group generated by hydrolysis of PAN, in addition to amides and amidines. It is worth to mention the release of ammonia during the degradation reaction, since it can be an important ligand to some radionuclides under the conditions of interest.
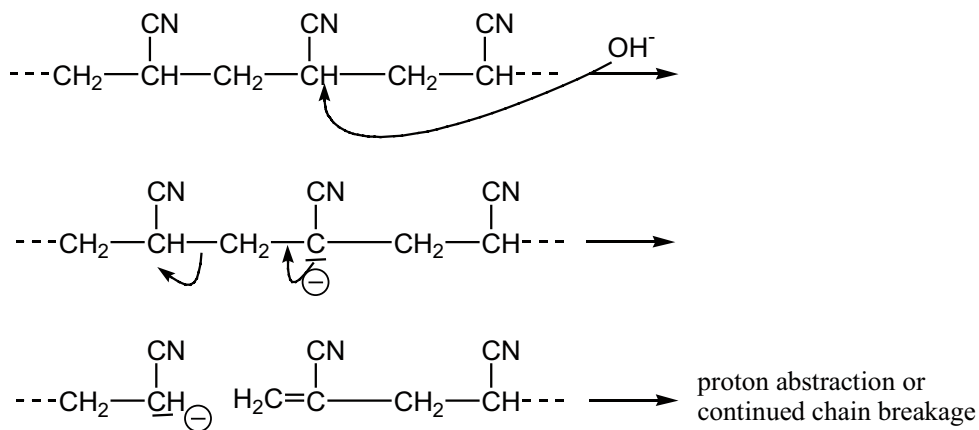
Figure 2-10. *The mechanism for depolymerisation of PAN in a basic solution.*
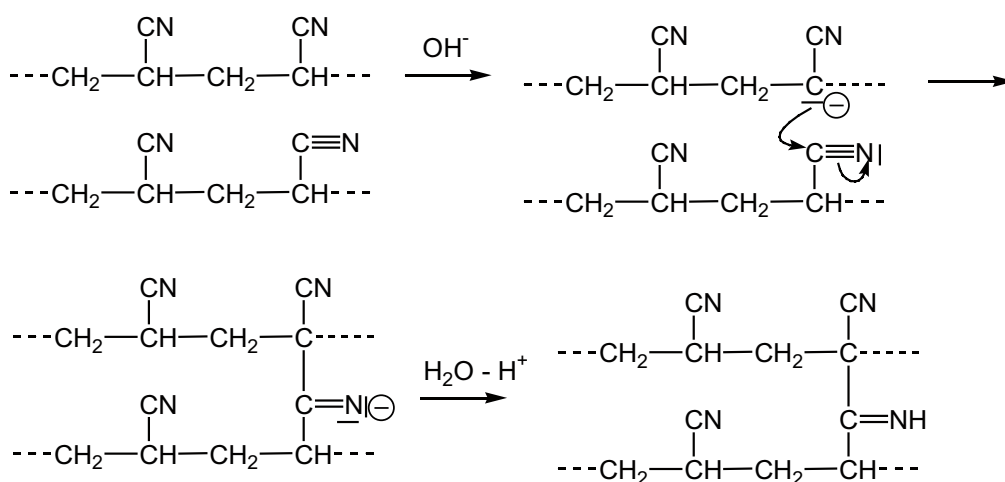

Figure 2-11. *Mechanism for the formation of crosslinking bonds in PAN in a basic solution.*
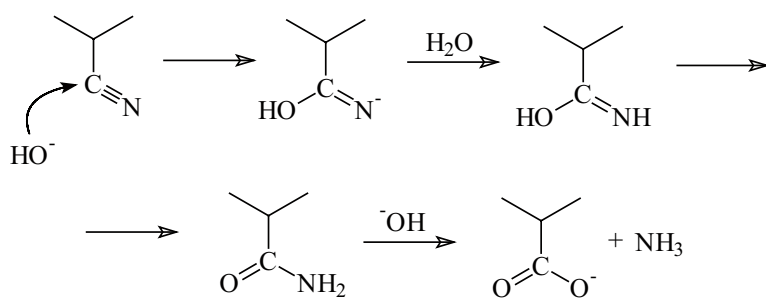

Figure 2-12. *Direct degradation of nitrile groups to carboxylates with ammonia release.*
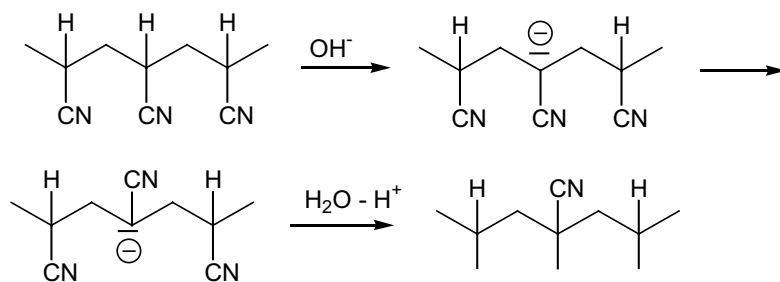

Figure 2-13. *Inversion of the configuration of PAN in a basic solution.*

The degradation mechanism in Figure 2-7 is accompanied by two collateral reactions that yield carboxylate and amide groups with, again, release of ammonia (Figure 2-12 and Figure 2-14).

The conjugated system existent during steps 2–8 of Figure 2-7 exhibits an important absorption (with maxima around 306 and 370 nm). In addition, Litmanovich and Platé (2000) studied the presence of amidines by NMR. From these experiments, it was observed that the loss of colour occurred with a proportion of amidines lower than 20%. Thus, degradation of the PAN polymer through conjugated amidines should not be neglected. Krentsel et al. (2001) manifested the validity of the proposed mechanism over a broad temperature range (25–85ºC).

During acidic hydrolysis of PAN with 65% nitric acid at 21°C, Krentsel et al. (2001) reports gradual hydrolysis of the nitrile groups to amides. They even showed that the reaction rate increased when the group next to the nitrile being hydrolysed was already an amide. They claim that less than 3% of the formed amides participate in cyclization reactions to form glutaric imides.

2.2.2 Thermal decomposition

Many studies have aimed to investigate the changes in polyacrylonitrile and which products are formed when the polymer is heated to high temperatures. This interest is due to the fact that carbon fibres can be manufactured in this way. Nevertheless, the temperatures in these studies are usually higher than those at which the polymer is used and dehydrated in connection with power plants.

Grassie and McGuchan (1972) heated PAN and PMAN to 500°C and could establish that the decrease in weight was 56%. The volatile compounds formed were ammonia, hydrogen cyanide and hydrogen. The decomposition products were the oligomeric structures that can be seen in Figure 2-15. It was further shown that PMAN and other polymers in which the α-carbon is substituted did not form oligomers but instead underwent depolymerisation. They claimed a radical reaction and pointed out the importance of the hydrogen atom on the α-carbon in stabilising the corresponding radical during the decomposition of PAN.

Kaykhaii et al. (2002) and Saufi and Ismail (2002) heated PAN to high temperatures (250–700ºC). Under these conditions, PAN carbonised by releasing its main nitrogen content as N_2 and some short-chain nitrile compounds.

Usami et al. (1990) studied the decomposition products from PAN with pyrolysis GC-MS (a pyrolysis unit on-line with a gas chromatograph and mass spectrometer) at 700°C. The main products were different mono-, di-, tri-, and tetramers of acrylonitrile (Figure 2-16). Since nitriles can be hydrolysed to carboxylic acids, the compounds in Figure 2-16 are potential mono-, di-, and tri carboxylic acids.
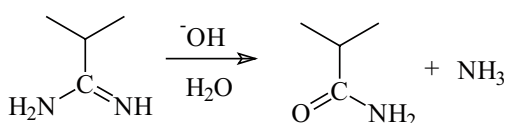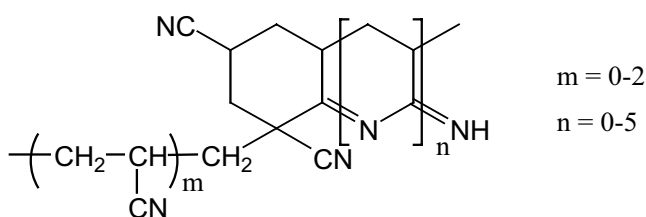

Figure 2-14. *Amidine hydrolysis.*

m = 0-2

n = 0-5

Figure 2-15. *General structure for oligomers of PAN during thermal decomposition.*

CH₃—CN CH₂=CH—CN CH₃—CH₂—CN

$$CH_3-CN \quad CH_2=CH-CN \quad CH_3-CH_2-CN \quad CH_2=\underset{CN}{\overset{CH_3}{C}}-CN \quad CH_3-\underset{CN}{\overset{CH_3}{CH}}$$

$$CH_3-\underset{Cn}{CH}-CH=CH-CN \qquad CH_2=\underset{CN}{C}-CH_2-\underset{CN}{CH}-CH_3 \qquad \underset{CN}{CH_2}-\underset{}{CH_2}-\underset{CN}{CH_2}$$

$$CH_2=\underset{CN}{C}-CH_2-\underset{CN}{CH_2} \qquad CH_2=\underset{CN}{C}-CH_2-\underset{CN}{C}=CH_2 \qquad CH_3-\underset{CN}{\overset{H}{C}}-CH_2-\underset{CN}{CH_2}$$

$$\underset{CN}{CH}=CH-CH_2-CH_2-\underset{CN}{CH_2} \qquad CH_2=\underset{CN}{C}-CH_2-CH=CH-\underset{CN}{CH_2}$$

$$CH_2=\underset{CN}{C}-CH=CH-CH_2-\underset{CN}{CH_2} \qquad CH_2=\underset{CN}{C}-CH_2-\underset{CN}{CH}-CH_2-\underset{CN}{CH_2}$$

$$CH_3-\underset{CN}{\overset{H}{C}}-CH_2-\underset{CN}{CH}-CH_2-\underset{CN}{CH_2} \qquad CH_3-\underset{CN}{\overset{H}{C}}-CH_2-\underset{CN}{CH}-CH_2-\underset{CN}{CH_2}$$

$$\underset{CN}{CH_2}-CH=CH-CH_2-\underset{CN}{CH}-CH_2-\underset{CN}{CH_2} \qquad \underset{CN}{CH_2}-CH_2-CH=CH-\underset{CN}{CH}-CH_2-\underset{CN}{CH_2}$$

$$\underset{CN}{CH_2}-CH_2-\underset{CN}{CH}-CH_2-\underset{CN}{CH_2} \qquad \underset{CN}{CH_2}-CH_2-\underset{CN}{CH}-CH=\underset{CN}{CH}$$

$$CH_3-\underset{CN}{CH}-CH_2-\underset{CN}{CH}-CH_2-\underset{CN}{CH_2} \qquad \underset{CN}{CH_2}-CH_2-\underset{CN}{CH}-CH_2-\underset{CN}{CH}-CH_3$$
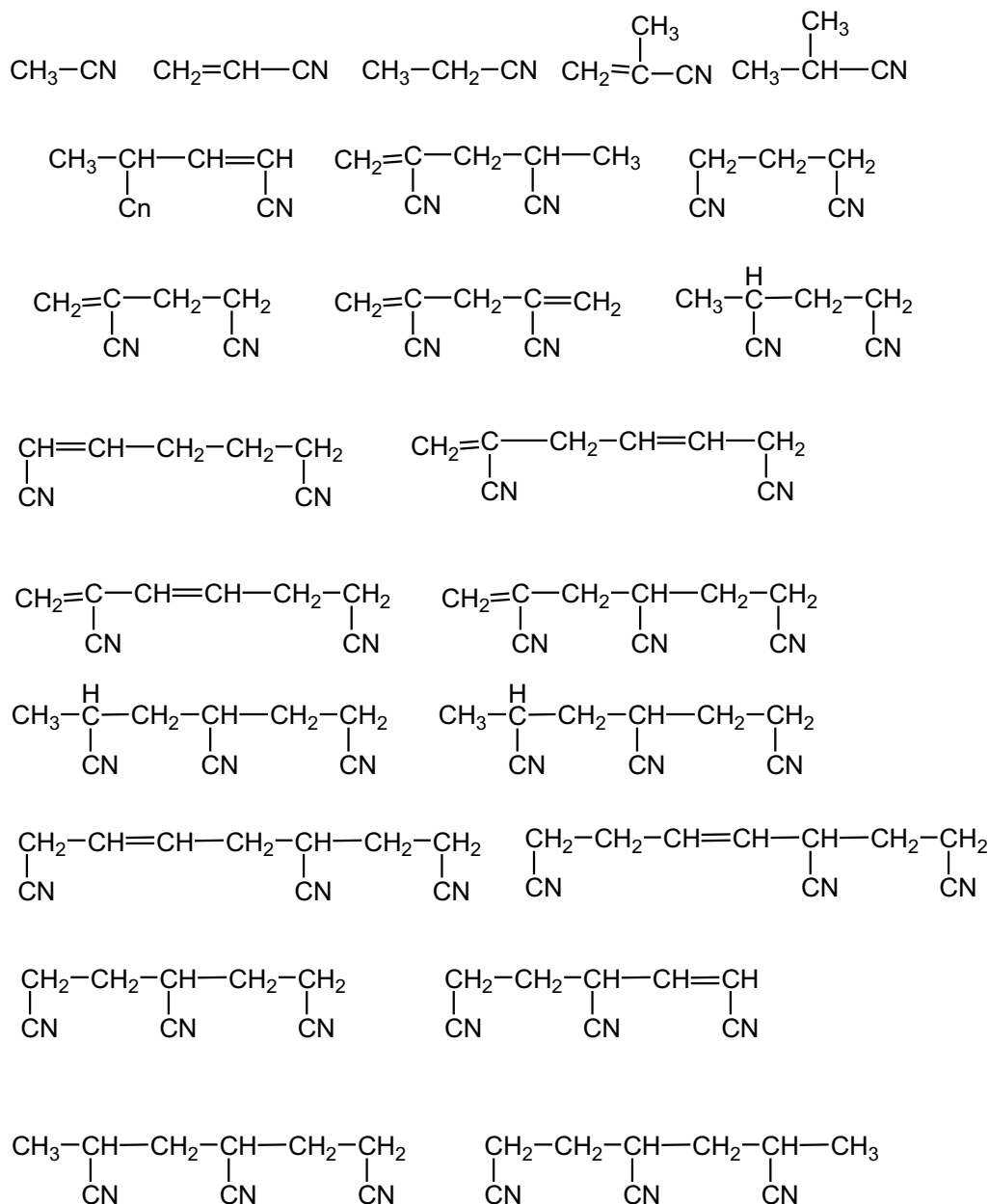
Figure 2-16. *Decomposition products from PAN at 700°C.*

During substantial heating of PAN carbon fibres are formed. Fitzer (1990) studied the formation and showed that PAN gradually was transformed to complicated polycyclic structures (Figure 2-17). If the reaction is continued large units of aromatic rings with structures similar to graphite are formed.

Surianarayanan et al. (1998) used ¹³C solid phase NMR and FT-IR to study thermal decomposition of PAN at 150–590°C. They found that PAN was stable at temperatures up to 150°C. At higher temperatures cyclization reactions gradually took place and larger complexes with gradually increased aromaticity were formed (Figure 2-18).

2.2.3 Radiolysis

Hill et al. (1992) studied the effects of γ-radiation on PAN with ESR-spectroscopy. At 300 K they could identify mainly two types of radicals. One, in which a hydrogen atom had left the methylene group in PAN and another when a radical had been added to the nitrile group (Figure 2-19). Both these radicals produced crosslinking bonds in the polymer, but not breakage of the chains of carbon.
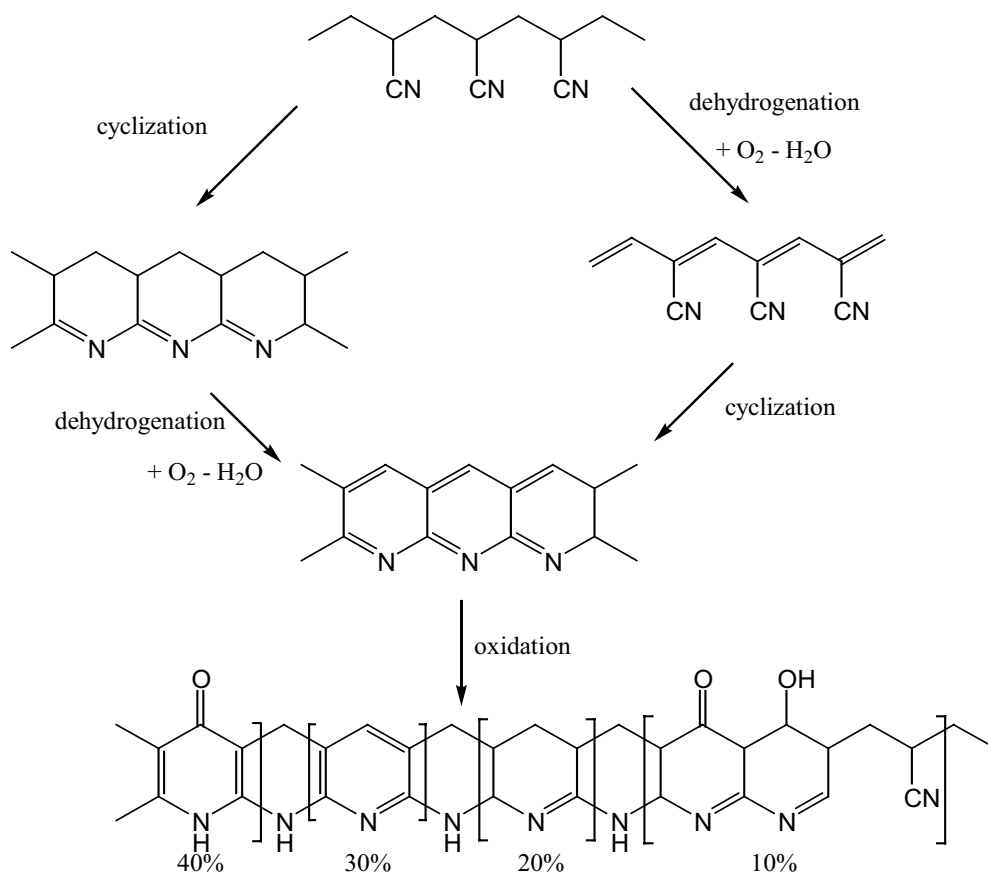
Figure 2-17. *Initial reactions in the formation of carbon fibres from PAN.*
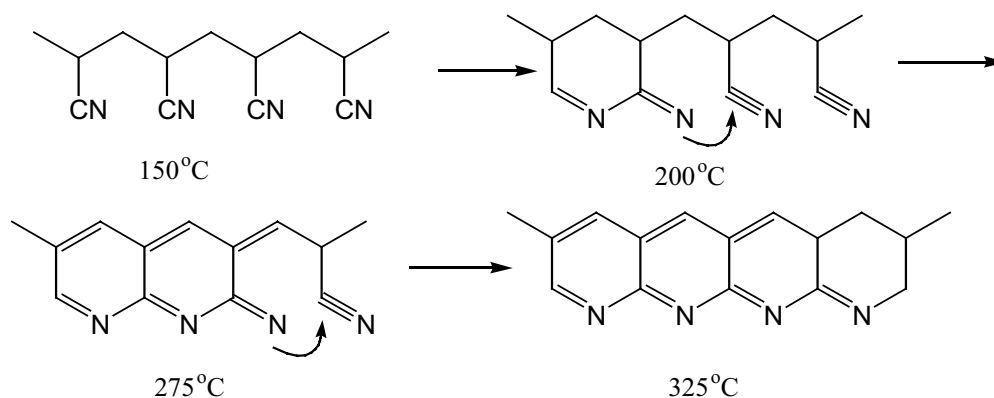
Figure 2-18. *Thermal decomposition of PAN.*

Figure 2-19. *Radicals that has been identified by radiolysis.*

Aggour and Aziz (2000) studied radiolysis of PAN with UV-radiation and with a low energetic argon beam. They found that the UV-radiation was less effective. With IR-spectroscopy they could identify new bands of NH, NH_2 and C=C groups. The reactions that PAN was involved in were the formation of new conjugated polyenes and intramolecular cyclization (Figure 2-20).
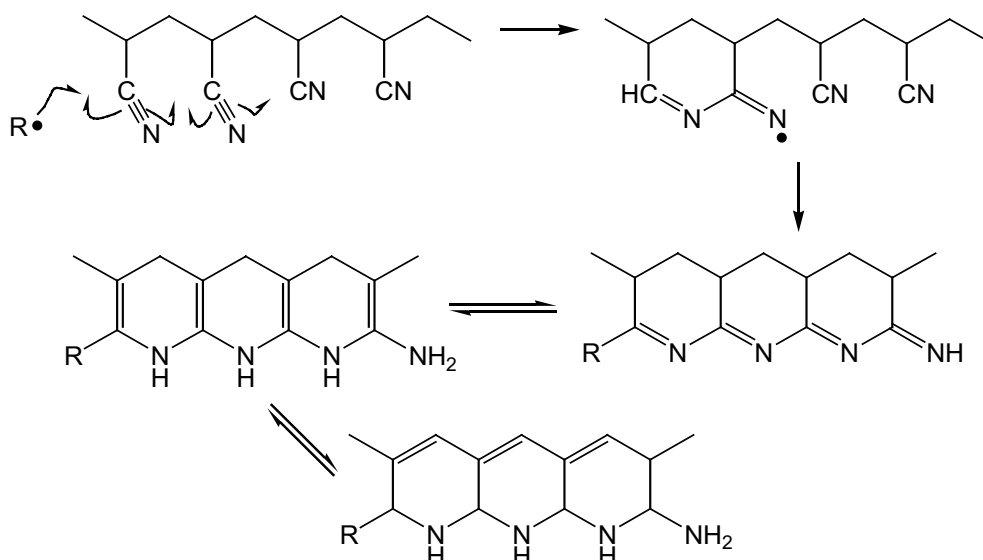
Figure 2-20. *Cyclization during radiolysis.*

2.2.4 Microbial decomposition

It is very difficult for microbes to decompose PAN. Gosavi et al. (1999) found that after hydrolysis with alkali bacteria could decompose a superabsorbent containing starch cross-linked to PAN. During the hydrolysis the nitrile groups in PAN were transformed to carboxylate groups and amides, and the bacteria could use the nitrogen atom in the amide group as the only nitrogen source.

2.2.5 Other decomposition studies

Howell and Patil (1992) exposed PAN to different climate influences. They studied the changes with IR-spectroscopy and GPC (gel permeation chromatography). They found clear indications on an increased amount of C=C, C=N and C=O bonds after the treatment. More over, they found considerably bigger differences between the sample and the reference if the IR spectrum was measured with attenuated total reflection, ATR, technique instead of transmissions spectroscopy. Their interpretation was that most of the changes occurred on the surface of the PAN and not in inside of the fibre. Furthermore, simultaneously as the molecular mass decreased significantly during the treatment, the molecular mass distribution became more heterogeneous.

2.3 Conclusions from the literature review

It is clear from the summaries given above that polyacrylonitrile is difficult to dissolve in water and that it is stable during normal chemical and physical conditions. The polymer endures temperatures up to 150°C. However, strong acids and bases affect the polymer. The most obvious effect is the formation of coloured complexes. These can have a very strong colour, but it is clear from the survey above that the content of these complexes is small. However, it is probable that other, not coloured, but crosslinked complexes are formed to a large extent. The water solubility ought to be decreased even more with these complexes. The conclusion is that PAN is affected only to a very limited extent during the conditions at which it is stored, used and dehydrated in power plants.

Some reactions will probably take place in the final repository. To a certain extent PAN will be crosslinked, which leads to a further decrease in the solubility and the reactivity. The nitrile groups will slowly be hydrolysed to amides and salts of carboxylic acids. Furthermore, it is probable that some depolymerisation or other decomposition reactions to low molecular units will take place. Since nitrile groups are derivates of acids, for many cases the reasonably final products from these reactions will be salts of carboxylic acids with varying ability to form metal complexes.

N,N-dimethylacetamide has a high water solubility. Therefore, the amount initially present in UP2 (max. 0.5% according to the manufacturer) will be washed out before UP2 is placed in the final repository.

3 Experimental study of UP2 degradation under conditions simulating both its usage in a power plant and disposal in a concrete repository

3.1 Introduction

Under normal operation in a nuclear power plant, UP2 is contaminated by radionuclides and consequently must be deposited as intermediate-level waste. During plant operation the UP2 fibre is treated at 65°C with water containing 15 ppb of Fe^{3+} and 5 ppb of hydrogen peroxide. After its use in the power plant, UP2 is dried at 150°C for 24 h and transported to a cementitious repository (SFR1).

During this study, representatives from the nuclear power plant in Ringhals also expressed interest in using UP2. The process at Ringhals is somewhat different from the standard procedure outlined above. In case Ringhals decided to use UP2, the fibre would be treated at 85°C with Fe^{3+} and hydrogen peroxide, and it would be dried at 105°C for 12 h. Therefore these conditions were also studied.

Since alkaline conditions are prevailing in the SFR1 repository, where the UP2 fibre will be deposited, the degradation of UP2 at pH 12.5 and different temperatures was also studied.

3.1.1 Aim of the experimental study

The present study on the degradation of UP2 was performed in three parts:

- conditions simulating its use in a nuclear power plant, followed by simulation of the drying process,
- conditions simulating a concrete repository with percolating water, and
- degradation under forced conditions (alkaline conditions at higher temperature).

The aim of the first part of this work was to study possible changes in the solid polymer, in order to decide whether the next part of the study (repository conditions) could be performed on UP2 fibre that was not pre-treated. In the case that UP2 undergoes structural changes either during its use in the nuclear power plant or during the drying process, the UP2 fibre to be studied under simulated repository conditions would have to be pre-treated prior to simulating these structural changes.

In the second part of the investigation the aim was to study water-soluble degradation products from the UP2 fibre under the alkaline conditions of a cement repository. In the last part the degradation rate under alkaline conditions was enhanced by increasing the temperature in order to obtain higher concentrations of degradation products to use in the sorption experiments described in Chapter 5.

3.2 Materials and methods

3.2.1 Degradation of UP2

Conditions simulating its use in a nuclear power plant and subsequent drying process

Alternative I (65°C): 10 g of UP2 were treated with 250 mL of a solution of 15 ppb of Fe^{3+} and 5 ppb of hydrogen peroxide in a round-bottomed flask. The flask was thermostat controlled in a water bath at 65°C. Twice a day the UP2 fibre was filtered off, the solution analysed by UV-spectroscopy and a fresh solution added to the UP2. After one month, the treatment was stopped and the UP2 fibre isolated by filtration. Part of the isolated fibre was freeze-dried to be analysed.

After treatment with Fe^{3+} and hydrogen peroxide at elevated temperature, UP2 was filtered off to be dried in a warming cupboard at 150°C for 24 h. Dry UP2 was analysed by FT-IR as a KBr-pellet. For NMR-analysis UP2 was dissolved in DMSO-D_6. Treated UP2 was compared with untreated UP2 fibre that was also freeze-dried.

Alternative II (85°C): In order to simulate the conditions at the Ringhals nuclear power plant, 10 g of UP2 were treated with Fe^{3+} and hydrogen peroxide for one month as described above, but at a temperature of 85°C. The UP2 fibre was then dried at 105°C for 12 h.

Conditions simulating a final nuclear repository

The UP2 fibre was treated with two different solutions:

- pH = 12.5: the solution contained $Ca(OH)_2$, 100 g/L. The concentration of sodium hydroxide was 11.4 mM and the concentration of potassium hydroxide 18.0 mM.

- pH = 13.4: this solution contained $Ca(OH)_2$ 100 g/L. The concentration of sodium hydroxide was 114 mM and the concentration of potassium hydroxide 180 mM.

The UP2 fibre was added to these solutions at a concentration of 25 g/L.

The solution at pH = 12.5, with added UP2 fibre, is called Sample I and the solution with pH = 13.4, with added UP2 fibre, is called Sample II.

For each sample solution there was a corresponding reference solution. The reference solutions were identical to the sample solutions but did not contain any UP2 fibre. The reference solutions are called Ref I (pH = 12.5) and Ref II (pH = 13.4).

All solutions were left at room temperature in the dark, with slow continuous stirring or alternatively, with vigorous discontinuous stirring for 23 months. Sub samples were collected after 4, 8, 15, 32, 63, 129, 276 and 694 days for DOC and UV-analysis.

Forced degradation conditions (higher temperature)

The UP2 fibre was mixed with water to a concentration of 50 g/L, the pH adjusted to 12.5 with NaOH and stored at 60°C for up to 97 days. The Ca^{2+} concentration was adjusted to 0 or 0.01 M. The solid phase was separated by centrifugation (24,500 g, 1 h) before analysing the soluble degradation products (DOC and its effect on radionuclide sorption).

3.2.2　Analysis

pH

The pH of the samples and reference solutions was measured at every sampling occasion, except for the samples from UP2-degradation under forced conditions, where only the final pH was measured.

DOC dissolved organic carbon

Sub samples from the study of the degradation under simulated repository conditions were filtered through a 0.4 μm polycarbonate filter, while the samples from the degradation study under forced conditions (high temperature) were centrifuged (24,500 g, 1 h). Samples for DOC-analysis were preserved by acidification with concentrated hydrochloric acid.

UV-spectroscopy

Sub samples were taken from all solutions for UV-spectroscopy. The samples were filtered through 0.4 μm polycarbonate membrane filters. UV-spectra were recorded of solutions at both high and low pH.

Direct gas chromatographic analysis of aqueous solutions

For the analysis of low-molecular-weight monocarboxylic acids, a gas chromatographic method was utilised (Jonsson and Borén 2002) with direct injection of an aqueous solution on a polar GC-column and detection by a flame ionisation detector. In order to eliminate inorganic salts the samples were passed through a weak cat-ion exchanger before analysis.

Capillary electrophoresis

Low-molecular-weight carboxylic acids were analysed by capillary electrophoresis with a diode array detector (DAD) (Hagberg et al. 2000). Before analysis, the samples were diluted 1:4 to minimize matrix effects.

Analysis of carboxylic acids after esterification

Low-molecular-weight carboxylic acids, in particular dicarboxylic acids, were analysed, after transformation into butyl esters (Kawamura and Kaplan 1987). In order to eliminate inorganic salts, the samples were passed through a weak cationic exchanger prior to esterification. The samples were evaporated to dryness, esterified and analysed by GC-MS. The detection limit for this technique was approximately 1 µg/L. For a few acids, e.g. oxalic acid, it was not possible to construct a calibration curve because the ion exchanger, despite careful washing, leaked oxalic acid.

Analysis of volatile compounds

Concentration of volatile organic compounds was performed by a dynamic stripping technique (Borén et al. 1982). Volatile compounds were purged with nitrogen at a temperature of 60°C and adsorbed onto a filter of activated carbon. The filter was extracted with dichloromethane and the extract analysed by GC-MS. The detection limit for this technique was approximately 10 ng/L.

3.3   UP2 degradation: Experimental results and discussion

3.3.1   Conditions simulating UP2 use in a power plant and subsequent drying: Alternative I (65°C)

Prior to treatment, the UP2 fibre was washed several times with water. The washing water was analysed with UV-spectroscopy. There was a significant difference between the spectra of the first and the last washing waters. The reason was that small particles, fines, passed through the filter, thus making the solution less transparent. However, the spectra did not indicate the presence of any UV-absorbing chromophores.

During treatment of UP2 simulating its use in a power plant the solution was changed twice a day. On several occasions the solutions were analysed by UV-spectroscopy. There were no signs of any UV-absorbing chromophores in the solutions.

Figure 3-1 shows FT-IR spectra of the following: a) non-treated UP2; b) the same fibre after treatment with Fe^{3+} and hydrogen peroxide; and c) after drying. Structural changes are effectively studied by IR-spectroscopy. In Figure 3-1, it is shown that spectra, after the different treatments, are almost identical. Information about functional groups may be obtained from the left part of the spectra with wave numbers above 1,500 cm^{-1}. The strong peak at 2,240 cm^{-1} corresponds to the triple bonds in the nitrile groups. The right part of the spectra with wave numbers below 1,500 cm^{-1} is called the fingerprint region. This part of the spectrum is very sensitive to minor structural changes. The fingerprint region in IR-spectroscopy is almost as unique for an organic compound as the fingerprint of a human being.

^{13}C NMR-spectra of non-treated and treated UP2 fibre are shown in Figure 3-2. The large group of peaks at 39.7 ppm corresponds to the carbon atoms in the solvent, D_6-DMSO (dimethyl sulfoxide, CD_3SOCD_3). The couplings to the deuterium atoms cause the septet of peaks. The spectra were proton decoupled, which implies that the hydrogen atoms do not split the carbon atoms in UP2 in the way the deuterium atoms influence the carbon atoms in DMSO. The peak at 120 ppm corresponds to the carbon atom in the nitrile group.

The peaks just over 30 ppm correspond to the methylene carbon atom (CH_2) and the group below 30 ppm corresponds to the methine carbon atom (CH).

The different groups of peaks are split. This is due to the different configuration that the carbon chain in PAN may adopt (isotactic and syndiotactic as previously shown in Figure 2-5). The different configurations give rise to somewhat different chemical shifts, as is seen from the different ppm-values marked for the respective peak. A careful analysis of the position of the different carbon atoms reveals that their chemical shifts differ slightly in the different spectra. This difference, however, is eliminated when the solvent, DMSO, is taken as a reference.

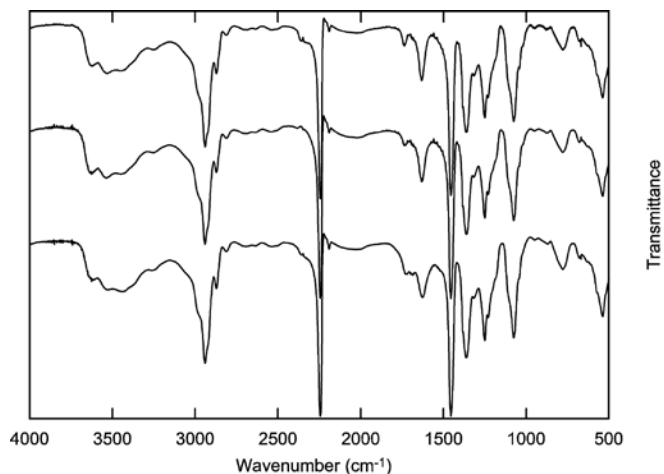**Figure 3-1.** *FT-IR-spectra of non-treated UP2 fibre (top spectrum), oxidized and heat-treated UP2 fibre (middle spectrum) and oxidized, heat-treated and dried UP2 fibre (lower spectrum), corresponding to Alternative I (65°C) conditions.*
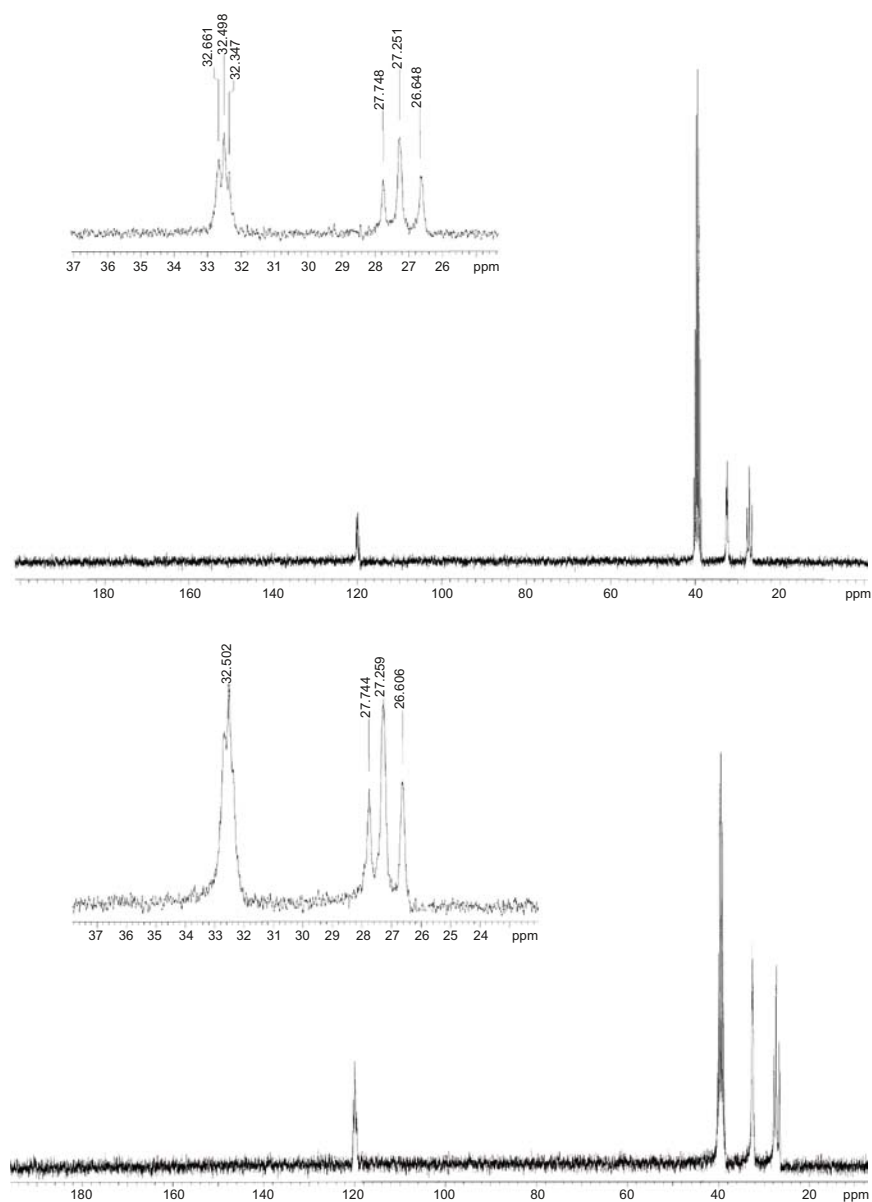

Figure 3-2. *^{13}C NMR spectra of non-treated UP2 fibre (top spectrum) and UP2 fibre treated with Fe^{3+} and H_2O_2 at 65°C and dried at 150°C for 24 h (lower spectrum).*

3.3.2 Conditions simulating UP2 use in a power plant and subsequent drying: Alternative II (85°C)

In Figure 3-3, it can be seen that the reasoning concerning the impact on the UP2 fibre under the conditions of alternative I (65°C) is true for the conditions used in alternative II (85°C) as well. However, in the lower spectrum in Figure 3-3 there are a few small peaks at 2,350 cm^{-1} that are missing in the other spectra. These peaks originate from carbon dioxide in the background spectrum, and it was hard to totally compensate for them. Consequently, the observed difference does not represent any structural change in the polymer.

The NMR-spectrum in Figure 3-4 represents a sample treated according to the conditions in alternative II. It should be compared to the upper spectrum in Figure 3-2, representing the non-treated sample. The results of both spectra are almost identical.

The main conclusion from the study of the UP2 degradation under conditions simulating its use in a nuclear power plant, followed by simulation of the drying process, is that no change could be observed for the fibre under these conditions.
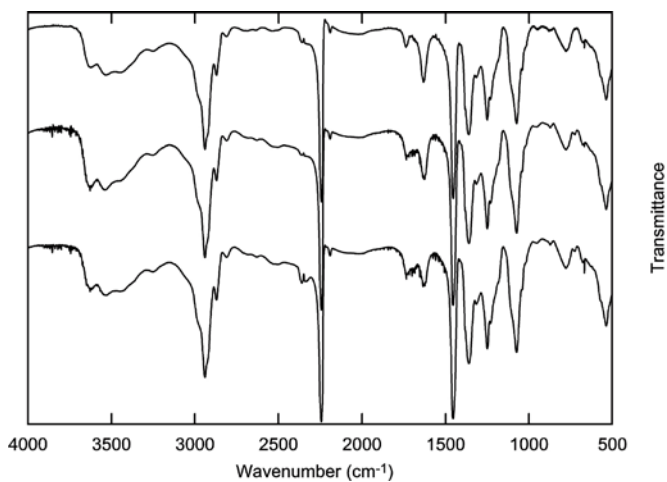

Figure 3-3. *FT-IR-spectra of non-treated UP2 fibre (top spectrum), UP2 fibre oxidized and heat-treated at 85°C (middle spectrum) and UP2 fibre oxidized, heat-treated and dried at 105°C, 12 h (lower spectrum).*
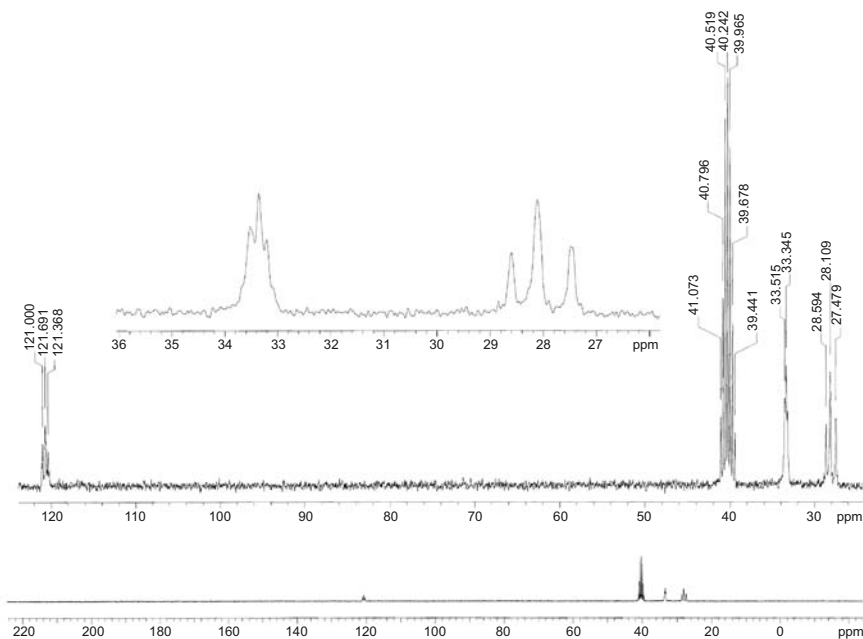

Figure 3-4. ^{13}C *NMR-spectrum of UP2 fibre treated with Fe^{3+}, H_2O_2 at 85°C and thereafter dried at 105°C for 12 h.*

3.3.3 Degradation under alkaline conditions: Simulation of repository conditions and forced conditions (60°C)

Analysis of pH

Table 3-1 shows the change in pH with time for the samples at room temperature. Only marginal changes were observed. There was no significant difference between reference solutions and sample solutions. i.e. solutions with and without added UP2 fibre. The pH of a sample kept at 60°C after 56 days was 12.3. The differences observed may be due to the difficulties in measuring higher pH-values.

DOC-analysis

In Table 3-2 and Figure 3-5, the evolution of the concentration of dissolved organic carbon with time is shown.

From Figure 3-5, it can be seen that, during the first weeks, DOC was increasing faster than in the later part of the experiment. This rapid increase in DOC was probably not a result of the UP2 fibre containing water-soluble constituents because the UP2 fibre was carefully washed before the start of the experiment. This assumption is also supported by the fact that the increase in DOC is different for the samples at pH ≈ 12.5 and at ≈ 13.4. The rapid increase should rather be interpreted as parts of the UP2 fibre containing compounds that were reactive with OH⁻, producing water-soluble components.

Table 3-1. pH-changes with time for the leachates.

	Day 1	Day 4	Day 8	Day 15	Day 32	Day 63	Day 129	Day 276	Day 694
Ref I	12.5	12.6	12.7	12.7	12.7	12.6	12.8	12.8	12.7
Ref II	13.4	13.4	13.3	13.3	13.3	13.2	13.3	13.3	13.3
Sample I	12.5	12.6	12.7	12.7	12.7	12.7	12.7	12.8	12.7
Sample II	13.4	13.4	13.3	13.3	13.4	13.2	13.3	13.3	13.3

Table 3-2. Evolution of DOC (mg/L) in the leachates with time.

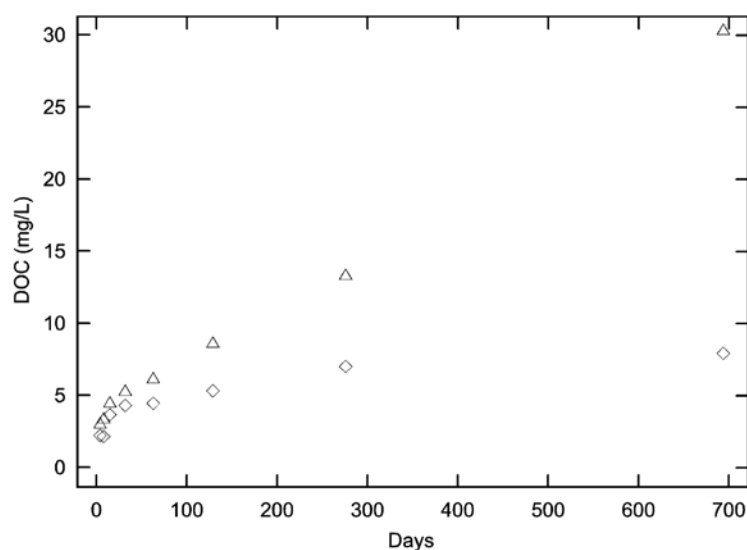| Sample	Day 4	Day 8	Day 15	Day 32	Day 63	Day 129	Day 276	Day 694
Ref I (pH ≈ 12.5)	1.0	1.8	1.1	1.0	0.8	1.4	a	1.5
Ref II (pH ≈ 13.4)	1.7	1.9	1.6	1.3	1.4	2.7	1.8	3.3
Sample I (pH ≈ 12.5)	3.2	3.9	4.8	5.3	5.2	6.7	8.2	9.4
Sample II (pH ≈ 13.4)	4.8	5.4	6.2	6.7	7.7	11.4	15.2	33.7

ᵃ The average of the references from day 4–129 is used.

Figure 3-5. *Change in DOC with time for the leachates at room temperature. (◊) Sample I – Ref I (pH ≈ 12.5); (Δ) Sample II – Ref II (pH ≈13.4).*

The DOC concentration of the solutions at pH ≈ 12.5 seemed to level off at a concentration of about 8 mg/L. From day 32 onwards, an almost linear increase in DOC by 1.2 mg/L per month for the solution at pH ≈ 13.4 is observed.

When analysing the DOC-results, the difficulty to measure low DOC-concentrations should be considered. The irregularity that can be observed in the left part of the curve and in the reference solutions may be an indication of that.

In Figure 3-6, the concentrations of DOC with time are displayed for the samples treated at pH ≈ 12.5 and 60°C. It is evident that the higher the temperature, the faster the degradation of the polymer. In addition, the presence of calcium more than doubled the formation of degradation products. In less than two months a 4.1% of the fibre (initially 50 g/L) was degraded to soluble substances.

UV-spectroscopy

In Figure 3-7, UV-spectra of the sample at room temperature and pH ≈ 13.4 and the corresponding reference solution are displayed. The spectra of samples and references are almost identical. No chromophores were identified in any spectrum. At short wavelengths, spectra show end-absorption and at longer wavelengths the solutions are transparent. In addition, there was no absorption in the visible region. Under the conditions used in the room temperature experiments, we cannot confirm the condensation products reported when PAN was treated in base (Karpacheva et al. 2000). The solutions obtained with forced conditions (pH ≈ 12.5, 60°C) became brown/yellow.
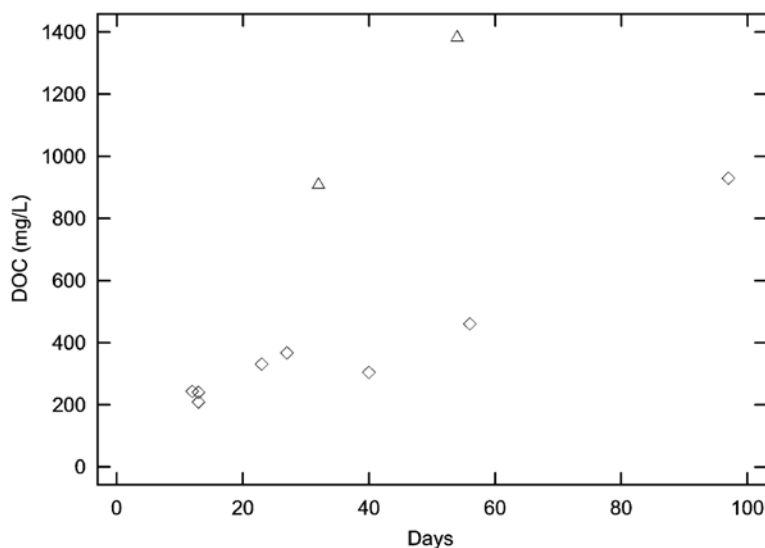

Figure 3-6. Change in DOC in the leachates at 60°C with time. (◊) [Ca] = 0 M; (△) [Ca] = 0.01 M.

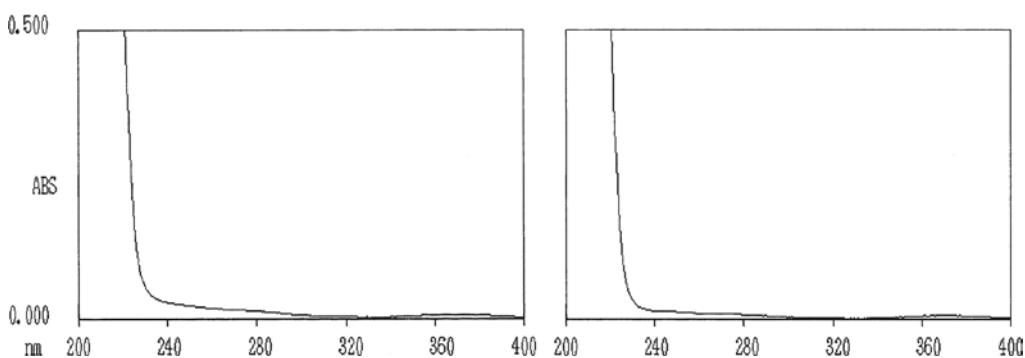*Figure 3-7.* UV-spectra of leachates from experiments at room temperature and at pH ≈ 13.4 (left) and the corresponding reference solution (right) after 129 days.

Direct gas chromatographic analysis of aqueous solutions

With this technique the sample solutions obtained at room temperature and pH ≈ 12.5 or pH ≈ 13.4 after 129 days of degradation, were analysed directly after passing through an ion exchanger without further concentration. Formic acid was added to acidify the samples and therefore formic acid was not analysed. The detection limit was as high as 1 mg/L. In an attempt to lower the detection limit, the sample was evaporated before injection in the gas chromatograph, but this only resulted in an increase in the background noise.

The result was that the concentrations of low-molecular-weight monocarboxylic acids were below the detection limit of 1 mg/L.

Capillary electrophoresis with DAD

The detection limit for capillary electrophoresis was approximately 0.5 mg/L. The calibration curves showed that the analysis worked well for concentrations above 0.5 mg/L. In the sample at pH ≈ 12.5 after 129 days of degradation, formic acid and acetic acid were identified by spiking. Formic acid was also found in the sample at pH ≈ 13.4 after 129 days of degradation together with an unidentified acid. The concentrations of the acids were low, just over the detection limit of the method.

The result was that low-molecular-weight carboxylic acids were not present in the samples at concentrations above 1 mg/L.

Analysis of carboxylic acids after esterificatiton

The technique used was developed for the analysis of carboxylic acids. However, in addition, some lipophilic compounds may be quantified by the same method. Many common compounds may also be found in the reference solutions when the detection limit is low. In Table 3-3, compounds also identified in the reference solutions are indicated by an asterisk. An internal standard, 2,4-dichlorbenzoic acid, was used for quantification. Area quotients, i.e. the area for a compound divided by the area of the internal standard, were calculated. For each compound in Table 3-3 the area quotients were at least three times that of the reference solution. For quantification, the area quotient of a compound in the reference solution was subtracted. Malonic acid and adipic acid were quantified by calibration curves. The other compounds were quantified by comparison with the internal standard. The structures of non-branched dicarboxylic acids were confirmed by references. For the other compounds, the suggestions by the library or our own spectra assignments were the basis of the given structures. All carboxylic acids were analysed as butyl esters, but they are given as free acids in Table 3-3.

None of the compounds in Table 3-3 has a chemical structure that can be directly derived from the structure of PAN. Aliphatic, as well as aromatic compounds are identified although, as far as we know, only aliphatic compounds were present in the UP2 fibre.

Analysis of volatile compounds

The compounds identified in the samples after concentration by stripping are shown in Table 3-4. None of these compounds has a direct relation to the PAN structure. Only a few volatile compounds were identified. The compounds present at highest concentrations were fatty acids. These acids were probably not present in the UP2 fibre as free acids but rather present as condensation products that were hydrolysed under the prevailing alkaline conditions.

Table 3-3. Compounds identified in leachates obtained at room temperature after 129 days, and quantified according to Kawamura and Kaplan (1987).

Ret. time (min)	Compound	Sample at pH ≈ 12.5 Conc. (µg/L)	Sample at pH ≈ 13.4 Conc. (µg/L)
12.40	3-hydroxybutanoic acid	150	130
13.36	1,2,3,4-tetrahydronaphtalene	2	20
14.58	p-nitrotoluene	2	11
18.93	4-phenyl-3-buten-2-one	230	1,900
21.53	malonic acid	5	220
22.17	methylmalonic acid	<1	69
25.23	glutaric acid	<1	53
25.64	2-hydroxy-2-phenyletanoic acid	<1	240
29.56	adipic acid	190	420
31.76	3-methyladipic acid	<1	37
36.76	1,5-diphenyl-1,4-pentadien-3-one	29	140
37.28	1,5-diphenyl-1-penten-3-one	29	200

Table 3-4. Volatile compounds from leachates at room temperature after 129 days analysed by dynamic stripping.

Ret. time (min)	Compound	Sample at pH ≈ 12.5 Conc. (ng/L)	Sample at pH ≈ 13.4 Conc. (ng/L)
4.68	2-hexanone	29	17
8.20	2-heptanone	400	320
12.04	2-octanone	420	450
15.66	2-nonanone	210	240
18.87	octanoic acid	280	1,000
18.99	2-decanone	62	86
24.80	2-bromo-4-tert.butylphenol	47	280
24.91	decanoic acid	1,100	8,400
29.87	dodecanoic acid	3,100	15,000
32.07	2,6-dibromo-4-tert.butylphenol	65	660
34.08	tetradecanoic acid	35	250
36.61	2,6-di tert.butyl-4-nitrophenol	18	39

3.4   Experimental study of UP2 degradation: Conclusions

In the first parts of the experimental study presented above, it was demonstrated that the solid UP2 fibre did not undergo any structural changes under the influence of the different conditions simulating those in a nuclear power plant including drying of the UP2 fibre. IR-spectra, as well as NMR-spectra of the UP2 fibre were almost identical before and after treatment.

From the last part of the study, it can be concluded that the concentration of dissolved organic carbon rapidly increased during the first weeks of the degradation experiments under alkaline conditions. The increase in DOC after the first weeks was almost linear and still remained so after 23 months for the sample at pH ≈ 13.4. In the sample at pH ≈ 12.5, there was almost no increase in DOC after 23 months. From the results obtained so far, we can calculate a 0.03% conversion of PAN into dissolved compounds after 23 months at pH ≈ 12.5 and a 0.12% at pH ≈ 13.4.

A number of different compounds were identified in the leachates of the UP2 fibre with various analytical techniques. That this is the result of the alkaline conditions is demonstrated by the fact that the compounds are almost exclusively present at higher concentrations in the solution with the highest pH. The identified compounds were mainly carboxylic acids, besides several low-molecular-weight lipophilic compounds such as 2-alkanones.

None of the compounds identified in the leachates has a direct relation to the main structure of PAN. No indications on the formation of condensed aromatic structures with a strong absorption in UV- or visible light were found. One reason for this is that the studies reported in the literature concerning the degradation of PAN in alkaline aqueous solution always utilised more extreme conditions than in the present study.

The suggested structures of Table 3-3 and Table 3-4 are, in a few cases, verified by analysis of reference compounds. The remaining structures represent the suggestions given by the mass spectrometric library or by expert judgement interpretations.

In this study an attempt was done to generally characterise the organic material, but quantification was supported by calibration curves only for a few compounds. Most of the compounds were quantified by comparison of peak areas with that of the internal standard. When using GC-MS-analysis, this usually gives an accuracy of about ±50%. Consequently, the analysis should be called semi-quantitative.

Only a minor fraction of the total organic carbon contained in the samples was identified. The sum of all compounds identified for the sample at pH ≈ 12.5 was 415 µg/L out of a total organic carbon of 5,300 µg/L (≈ 8%) while when working at pH ≈ 13.4 this figure increases to ≈ 28% (2,450 µg/L out of 8,700 µg/L). It should be underlined that there is a major uncertainty in these figures.

The degradation products of UP2 expected to have a largest impact on radionuclide mobility are carboxylic acids and amides. The oxygen atom is the main electron donor in the organic complexants of interest here. A summary of the organic ligands identified in the UP2 fibre degradation under alkaline conditions is presented in Table 3-5.

Complexes with monodentate ligands are usually less stable than those with multidentate ligands. More importantly, the degree of complexation decreases more strongly with dilution for monodentate complexes than for multidentate complexes or chelates (Stumm and Morgan 1996). Ketones, phenols and amidines may be disregarded when looking at possible radionuclide complexing effects. Ketones and phenols have been detected in very small concentration (ppt), while amidine groups will not be stable once removed from its positions within the polymeric chain (Litmanovich and Platé 2000).

Table 3-5. Classification of the identified degradation products of the UP2 fibre.

Group	Ligands (organic compounds)
Monocarboxylic	3-hydroxybutanoic acid
	octanoic acid
	decanoic acid
	dodecanoic acid
	tetradecanoic acid
	acetic acid [†]
Dicarboxylic	malonic acid
	adipic acid
Ketone	4-phenyl-3-buten-2-one
	1,5-diphenyl-1,4-pentadien-3-one
	1,5-diphenyl-1-penten-3-one
	2-hexanone
	2-heptanone
	2-octanone
	2-nonanone
	2-decanone
Phenol	2-bromo-4-tertbutylphenol
	2,6-dibromo-4-tertbutylphenol
	2,6-ditertbutyl-4-nitrophenol
Amine	ammonia [‡]

†: From acetamide.
‡: From hydrolysis reactions, cf. Figure 2-12 and Figure 2-14.

4   Model for UP2 degradation kinetics

The assessment of the maximum concentration of UP2 degradation products generated in the repository requires a model of the kinetics of degradation. The comparison between the kinetics of the process and the residence time of water in the vaults will give some hints on the maximum concentration of degradation products remaining within the waste.

The results of the experimental study of the kinetics of degradation of UP2 under the conditions of interest for the SFR1 repository are discussed in the previous chapter. From the experimental data presented in Figure 3-5, a logarithmic dependence of [TOC] with time is shown. Such a type of time dependence is usually the result of several parallel and competitive elemental processes taking place in the system. The reasoning behind this dependence is easier to conceptualise when considering all the conditions that apply to the experimental results:

• [TOC] is, in this case, an over-all measurement, where all organic degradation products are summed up and, therefore, it cannot respond to a unique kinetic reaction.

• The occurrence of parallel and sequential reactions in a system produces a fairly complicated dependence on the rate of reaction with the individual component concentrations (for further insights in the model the reader is referred to Stone and Morgan 1990 and references therein). An example of the evolution of two different products result of parallel reactions is shown in Figure 4-1.

In Figure 4-2 the linear dependence of log(rate) with the reciprocal of the concentration of total organic carbon is shown.

The expression shown in Figure 4-2, when applied to the laboratory system, produces the description of the data shown in Figure 4-3. The empirical equation derived for the evolution of the [TOC] with time reproduces, within an acceptable range of uncertainty, the experimental results in the studied time-frame. Subsequently, the study of the time-evolution of this variable under repository conditions will be based on the model used to explain the available experimental data.

Although the last experimental point at pH $\approx$ 13.4 in Figure 4-3b falls above the simulated line, for the modelling purposes only data at pH $\approx$ 12.5 are considered and, therefore, no further attempts were conducted to better describe the data at pH $\approx$ 13.4.
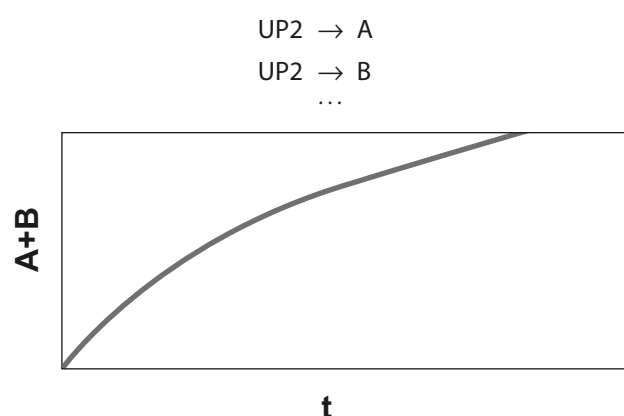

Figure 4-1. *Logarithmic dependence of the sum of two different products, originated through competitive or parallel reactions from the same reactant, with time.*
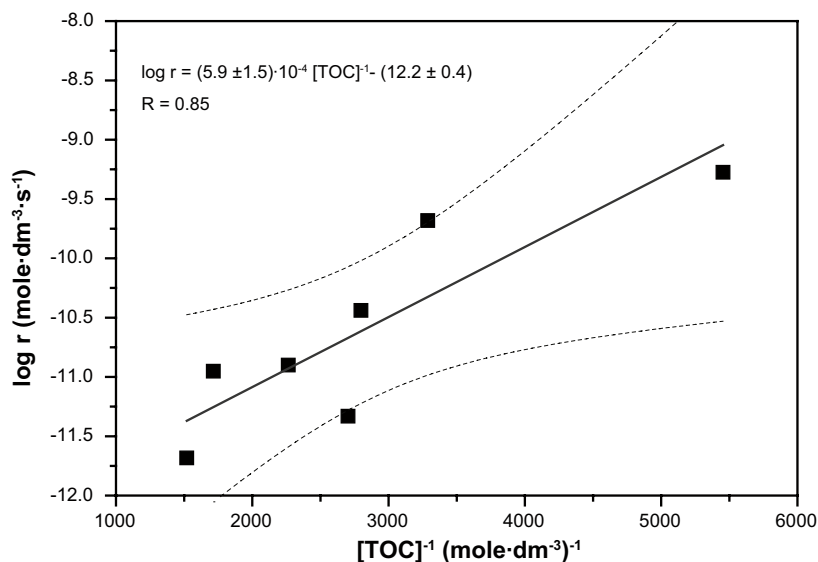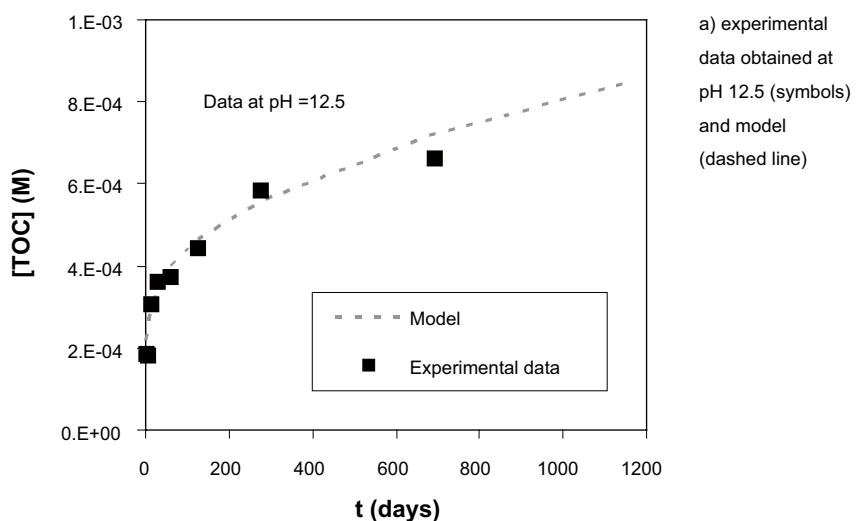
Figure 4-2. *Experimental degradation kinetics of UP2 fibre (points) and calculated degradation kinetics (lines) in terms of [TOC] generated along the time degradation. Data obtained at [UP2]$_0$ = 25 g/L, pH ≈ 12.5 and at room temperature. Dashed line stands for 98% confidence interval.*
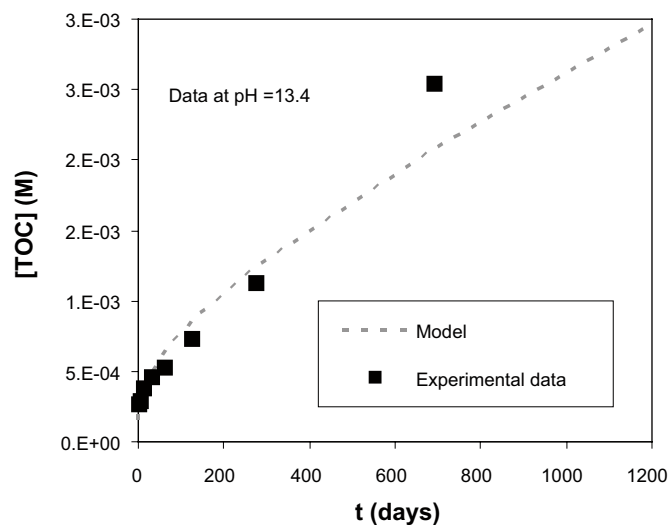
Figure 4-3. *Comparison between the empirical expression obtained for the rate law dependence with [TOC] and experimental data. a) pH = 12.5; b) pH = 13.4.*

5 Effect of the degradation products of UP2 on Eu sorption under alkaline conditions

In this section the results on the experimental investigation of the effect of UP2 degradation products on the sorption of Eu^{3+} as model radionuclide onto different solid substrates, TiO_2 and cement, are presented.

5.1 Materials and methods

To minimize the effect of the presence of carbonate in the system, sample preparation was performed in a glove-box under nitrogen atmosphere. The carbonate concentration in the samples was estimated to be below 2×10^{-5} M. Chemicals used in the experiments were of analytical grade. Water was purified by a Milli-Q apparatus (Millipore Corp.), slightly acidified and heated to reduce the carbonate concentration. All containers were leached with acid (3 M HNO_3, 0.1 M HCl) for at least 15 h and rinsed with Milli-Q water.

Exposure to light was avoided to prevent further degradation of the UP2 degradation products. Titanium dioxide can act as a photocatalyst thus increasing the rate of degradation of the organic complexing agents (Bangun and Adesina 1998, Kosanic 1998).

The experiments were not carried out under strictly sterile conditions, because Nordén (1994) performed similar experiments at pH 11-13 and found no microorganisms after 186 days.

The ionic strength was fixed at 0.3 M ([NaOH]+[NaCl]+3[CaCl$_2$] = 0.3 M), pH was 12.5 (12.3–12.7) and the solid to liquid ratio was 1 g/dm³ in all experiments. The temperature was kept at room temperature (20±2°C).

The experiments were carried as follows: about 0.02 g of the solid phase (either TiO_2 or cement) were weighed into 50 mL screw-capped polyallomer centrifuge tubes (Nalge), that were then transferred to the glove-box. Milli-Q water, NaOH to adjust pH, NaCl to adjust ionic strength, and Ca^{2+} (0 or 2 mM in the TiO_2 systems; 0 mM in the cement systems) were added. In most samples an amount was added of soluble UP2 degradation products, obtained under alkaline conditions as described in Chapter 3. The total volume of the samples varied with the amount of solid phase to keep a solid to liquid ratio of 1 g/dm³. The tubes were shaken and left overnight. The next day Eu^{3+} (final concentration in the centrifuge tube: 10^{-8} M) was added and the tubes were placed in a rotary tumbler for 24 h. The solid phase was separated from the solution by centrifugation (3,900 g, 30 min to separate TiO_2 and 24,500 g, 60 min to separate cement). An aliquot of the supernatant, 8 mL, was transferred to another tube and the amount of Eu^{3+} in solution was determined as described below. The pH was measured in the remaining part of the aqueous phase using a combination electrode (Radiometer Copenhagen, PHC 2412). The electrode was calibrated, using solutions of NaOH and NaCl. The total Na concentration was 0.3 M in the electrode calibration solutions as in the sorption experiments in order to compensate for sodium error.

Some tubes were left for up to 420 days to monitor the variation of sorption with time. These tubes were handled as the 24 h samples, except for the following. The total volume was about 30 mL (instead of 20 mL). However, the initial solid to liquid ratio was also kept at 1 g/dm³. The tubes were shaken in a rotary tumbler for 15 min three times a week. A continuous shaking could have a mechanical influence on the solid phase and therefore the amount of surface where sorption takes place. Analyses were performed after 1, 14, 28, 56, 112, 168, 252 and 420 days. At these occasions the tubes were centrifuged and a 2 mL aliquot of the supernatant was subtracted and analysed with respect to Eu. In order to re-suspend the solid phase in the remaining of the aqueous phase, the tubes were then shaken over night. After this, the standard three 15-min shaking per week was continued. Due to the small sample volume for Eu^{3+} measurement, the highest measurable K_d was $10^{3.4}$ m³/kg.

5.1.1 Eu³⁺

Radioactive ^{152}Eu^{3+} (Amersham) and Eu^{3+} carrier were mixed to get appropriate concentrations and activities. Eu^{3+} solutions contained at least 0.01 M HCl to avoid sorption to the vessel walls and precipitation. All Eu^{3+} concentrations were determined by counting the γ-activity (LKB Wallac 1282 Compugamma).

5.1.2 NaOH

A 50% w/w NaOH solution was filtered through a fibre-glass filter to remove carbonate as $Na_2CO_3(s)$. The filtrate was diluted and the concentration determined by titration of potassium hydrogen phthalate.

5.1.3 Titanium dioxide

TiO_2 (Feinchemikalien und Forschungsbedarf GmbH, Karlsruhe) used in the sorption experiments was a powder with a particle size lower than 1 μm (estimated from SEM pictures), a purity of 99.5% and a BET (N$_2$) surface area of 8.40 m²/g. With an assumed site density of 12.5 sites/nm² (Sahai and Sverjensky 1997), the surface was never saturated with Eu. X-ray diffraction analysis showed that the TiO_2 consisted of anatase only. The TiO_2 was washed with a solution of 0.1 M HCl and 0.2 M NaCl and rinsed with 0.3 M NaCl at a pH of 9. The solid phase was separated from the solution by centrifugation (353 g, 10 min). The rinsing was regarded as complete, when pH of the supernatant was 7-8. Then the TiO_2 was rinsed with water once and dried for 6 days at 80°C and 1 day at 130°C.

5.1.4 Cement

Standard Portland cement was cast in 40 mm acrylonitrilebutadienestyrene copolymer tubes. The ratio of cement to water was 2:1 by weight. After 1 day, the tubes were placed under water (to protect the cement from CO_2) during 120 days. Then the cement was crushed and sieved. The fraction less than 0.125 mm was used in the experiments. The surface area was 9.34 m²/g as determined by the BET (N$_2$) method.

5.2 Sorption experiments: Experimental results and discussion

In Figure 5-1 the change in K_d with time is presented. The solutions were left for more than a year and the concentration of Eu^{3+} in the solutions was measured at different time intervals. One sample was studied at two different concentrations, 3.62 and 36.2 mg/L DOC.

For all samples but the one obtained at room temperature, the trend showed an increase in K_d with time. This demonstrated that short time measurements will give the result of the worst possible situation. The same result is found for many other organic complexing agents (Dario et al. 2004a), where the log K_d reaches a constant value after some months. The sample obtained at room temperature showed an irregular distribution with time. The reason for this is not known.

In Figure 5-2, K_d is plotted against the concentration of DOC. The data show the following trends:

- TiO_2 was a stronger adsorbent for Eu(III) than cement.

- At DOC > 1 mg/L there was a measurable decrease in the retention of Eu^{3+} by the solid phases studied at pH 12.5. This effect may be attributed to the complexing ability of the degradation products of UP2. At higher concentrations of DOC there was an approximately linear effect on the decrease of Eu^{3+} sorption.

- The degradation of UP2 as described in Chapter 3 at room temperature and pH ≈ 13.4 resulted in DOC with higher complexing capacity than that obtained at pH ≈ 12.5.

- When all other conditions are the same, the DOC that had been obtained from UP2 degradation at 60°C in the presence of calcium showed a stronger complexing capacity.
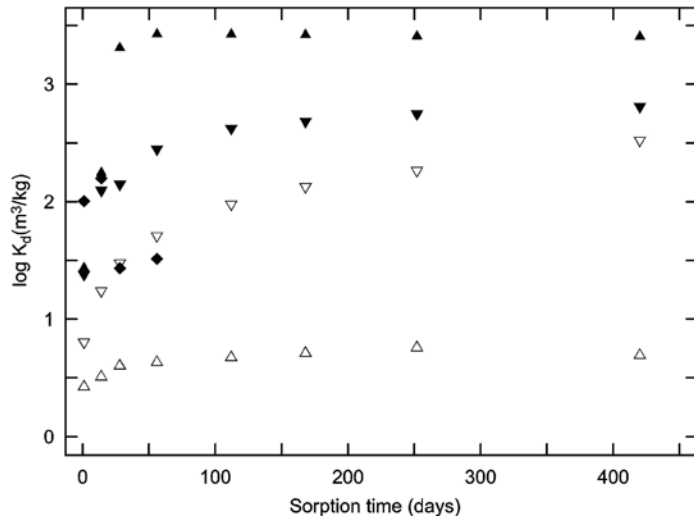
Figure 5-1. *Change of K_d with time for the sorption of Eu^{3+} on TiO_2 and cement.*

(∇) *TiO_2; [DOC] = 36.2 mg/L.*
($\blacktriangledown$) *TiO_2; [DOC] = 36.2 mg/L; [Ca]=2 mM (added in the sorption experiment).*
($\triangle$) *Cement; [DOC] = 36.2 mg/L.*
($\blacktriangle$) *Cement; [DOC] = 3.62 mg/L.*
($\blacklozenge$) *Cement; [DOC] = 10.7 mg/L.*

DOC was obtained by degradation of UP2 at pH ≈ 12.5, 60°C and no Ca2+ added, except for the sample with DOC 10.7 mg/L, which was obtained by UP2 degradation at room temperature and at pH ≈ 13.4.
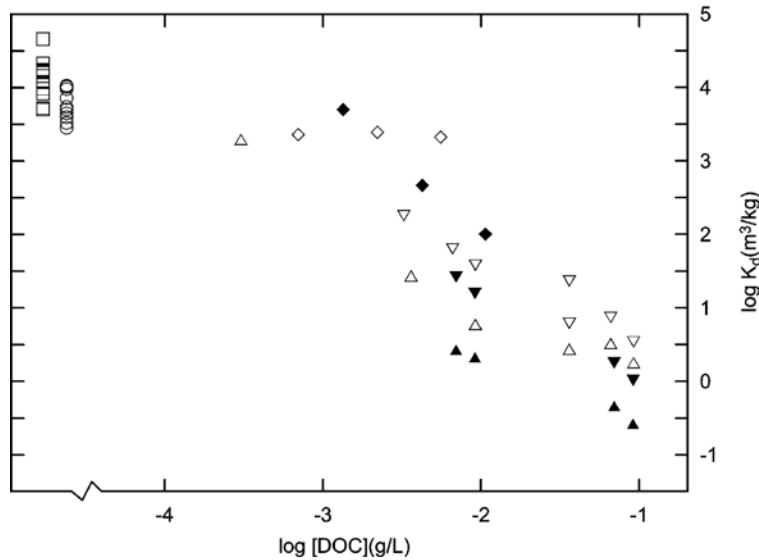

Figure 5-2. *K_d versus concentration of DOC (UP2 degradation products) for Eu^{3+} sorption on TiO_2 and cement. Sorption time: 1 day; pH 12.5; [Eu]=10^{-8} M.*

TiO_2:   ($\square$) *no added DOC.*
          (∇) *DOC obtained at 60°C and pH 12.5.*
          ($\blacktriangledown$) *DOC obtained at 60°C, pH 12.5 and [Ca]=0.01 M.*

Cement: ($\bigcirc$) *no added DOC.*
          ($\triangle$) *DOC obtained at 60°C and pH 12.5.*
          ($\blacktriangle$) *DOC obtained at 60°C, pH 12.5 and [Ca]=0.01 M.*
          ($\lozenge$) *DOC obtained at room temperature after 276 days, with UP2 in solutions saturated with Ca(OH)₂ at pH 12.5.*
          ($\blacklozenge$) *DOC obtained at room temperature after 276 days, with UP2 in solutions saturated with Ca(OH)₂ at pH 13.4.*

The DOC degradation at room temperature was always performed in alkaline solutions saturated with Ca(OH)₂.

5.3   Sorption experiments: Conclusions

The sorption experiments conducted att different DOC concentrations, figure 5-2, shows that the sorption of Eu^{3+} upon cement is not significantly affected at the DOC levels expected from degradation of UP2 8 mg/l at relevant SFR conditions pH=12.5, $[Ca^{2+}]$=0,01 M. The results are within the lower limit of the results obtained without any added DOC, figure 5-2.

At pH 13.5 the sorption of Eu^{3+} on cement is effected with almost 1.5 log units going from concentrations from 10^{-3} g/l to 10^{-2} g/l.

6 Summary and conclusions

The material filter UP2 degrades under hyper-alkaline conditions through several complex mechanisms to produce a set of low molecular weight organic compounds of difficult identification by the most advanced analytical techniques currently available.

Only a 20% of the produced degradation species have been identified, what poses some uncertainty on the assessment of the effect of these ligands on the behaviour of radionuclides in the presence of UP2.

The assessment of that effect has, therefore, been investigated by working with real UP2 degradation products and by developing conceptual models based on the combined effect of the mixture of degradation products formed.

The rate of degradation of UP2 follows a logarithmic function with the inverse of the concentration of the degradation products formed.and an empirical expression has been adopted to reproduce the experimental trend and for further application to repository conditions.

The sorption experiments conducted att different DOC concentrations shows that the sorption of Eu^{3+} upon cement is not significantly affected at the DOC levels expected from degradation of UP2 8 mg/l at relevant SFR conditions.

References

SKB's (Svensk Kärnbränslehantering AB) publications can be found at www.skb.se/publications.

Aggour Y A, Aziz M S, 2000. Degradation of polyacrylonitrile by low energy ion beam and UV radiation. Polymer Testing 19, 261–267.

Bajaj P, Chavan R B, Manjeet B, 1985. Saponification kinetics of acrylonitrile terpolymer and poly-acrylonitrile. Journal of Macromolecular Science A 22, 1219–1239.

Bangun, J, Adesina A A, 1998. The photodegradation kinetics of aqueous sodium oxalate solution using TiO_2 catalyst. Applied Catalysis A 175, 221–235.

Bashir Z, Manns G, Service D M, Bott D C, Herbert I R, Ibbett R N, Church S P, 1991. Investigation of base-induced cyclization and methine proton abstraction in polyacrylonitrile solutions. Polymer 32, 1826–1833.

Batty N S, Guthrie J T, 1981. A study of the origins of color in alkali degraded polyacrylonitrile and polymethacrylonitrile. 3. Computer predicted structures for the degradation products. Macromolecular Chemistry and Physics 182, 71–79.

Borén H B, Grimvall A, Sävenhed R, 1982. Modified stripping technique for the analysis of trace organics in water. Journal of Chromatography A 252, 139–146.

Bradbury M H, van Loon L R, 1997. Cementitious near-field data bases for performance assessment of a L/ILW repository in a Palfris marl host rock. PSI Report 98-01, Paul Scherrer Institut, Switzerland.

Campbell I M, 1994. Introduction to synthetic polymers. Oxford: Oxford University Press.

Dario M, Molera M, Allard B, 2004a. Effect of organic ligands on the sorption of europium on TiO_2 and cement at high pH. SKB TR-04-04, Svensk Kärnbränslehantering AB.

Dario M, Molera M, Allard B, 2004b. Effect of technical adsorbents and cleaning agents in a cement matrix : a case study. In Oversby V M, Werme L O (eds). Scientific basis for nuclear waste management XXVII: symposium held in Kalmar, Sweden, 15–19 June 2003. Warrendale, PA: Materials Research Society. (Materials Research Society Symposium Proceedings 807), 371–376.

Ermakov I V, Rebrov A I, Litmanovich A D, Platé N A, 2000. Alkaline hydrolysis of polyacrylonitrile, 1. Structure of the reaction products. Macromolecular Chemistry and Physics 201, 1415–1418.

Fitzer E, 1990. Polyaromaten mit Fasertextur – Die modernen Hochleistungs-Carbonfasern. Acta Polymerica 41, 381–389.

Gosavi U R, Deopurkar R L, Ghole V S, 1999. Microbial degradation of superabsorbent HSPAN gel by an indigenously isolated bacterial culture. Macromolecules 32, 4264–4271.

Grassie N, McGuchan R, 1972. Pyrolysis of polyacrylonitrile and related polymers V. Thermal analysis of α-substituted acrylonitrile polymers. European Polymer Journal 8, 243–255.

Gupta M L, Gupta B, Oppermann W, Hardtmann G J, 2004. Surface modification of polyacrylonitrile staple fibers via alkaline hydrolysis for superabsorbent applications. Journal of Applied Polymer Science 91, 3127–3133.

Hagberg J, Dahlén J, Karlsson S, Allard B, 2000. Application of capillary zone electrophoresis for the analysis of low molecular weight organic acids in environmental samples. International Journal of Environmental Analytical Chemistry 78, 385–396.

Hill D J T, Land A P, O'Donnell J H, Pomery P J, 1992. The effects of γ-radiation on polyacrylonitrile. Polymer Degradation and Stability 38, 193–203.

Holgersson S, Albinsson Y, Allard B, Borén H, Pavasars I, Engkvist I, 1998. Effects of gluco-isosaccharinate on Cs, Ni, Pm and Th sorption onto, and diffusion into cement. Radiochimica Acta 82, 393–398.

Howell H E, Patil A S, 1992. Analytical characterization of weather-degraded polyacrylonitrile fiber. Journal of Applied Polymer Science 44, 1523–1529.

Jonsson S, Borén H, 2002. Analysis of mono- and diesters of o-phtalic acid by solid-phase extractions with polystyrene-divinylbenzene-based polymers. Journal of Chromatography A 963, 393–400.

Karpacheva G P, Zemtsov L M, Bondarenko G N, Litmanovich A D, Platé N A, 2000. Formation of conjugated C=N bonds and their transformation in the alkaline hydrolysis of poly(acrylonitrile). Polymer Science A 42, 620–625.

Kawamura K, Kaplan I R, 1987. Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air. Environmental Science & Technology 21, 105–110.

Kaykhaii M, Sarafraz-Yazdi A, Chamsaz M, Pawliszyn J, 2002. Membrane extraction with sorbent interface-gas chromatography as an effective and fast means for continuous monitoring of thermal degradation products of polyacrylonitrile. Analyst 127, 912–916.

Kosanic M M, 1998. Photocatalytic degradation of oxalic acid over TiO_2 power. Journal of Photochemistry and Photobiology A: Chemistry 119, 119–122.

Krentsel L B, Kudryavtsev Y V, Rebrov A I, Litmanovich A D, Platé N A, 2001. Acidic hydrolysis of polyacrylonitrile: effect of neighboring groups. Macromolecules 34, 5607–5610.

Kudryavtsev Y V, Krentsel L B, Bondarenko G N, Litmanovich A D, Platé N A, Schapowalow S, Sackmann G, 2000. Alkaline hydrolysis of polyacrylonitrile, 2. On the product swelling. Macromolecular Chemistry and Physics 201, 1419–1425.

Ledin A, Karlsson S, Allard B, 1993. Effects of pH, ionic strength and a fulvic acid on size distribution and surface charge of colloidal quartz and hematite. Applied Geochemistry 8, 409–414.

Litmanovich A D, Platé N A, 2000. Alkaline hydrolysis of polyacrylonitrile. On the reaction mechanism. Macromolecular Chemistry and Physics 201, 2176–2180.

Nordén M, 1994. The complexation of some radionuclides with natural organics: implications for radioactive waste disposal. PhD thesis. Linköping University, Sweden.

Ochs, M.; Lothenbach, B.; Hager, D.; Helfer, S.; Wierczinski, B. and Skarnemark, G, 1997. Solubility limits and asorption reactions. Experimental and Theoretical investigation on the behaviour of Sn, Ni, eu(Am), Pb, Re(Tc), Th, Sr and Cs in Cementitious systems. ANDRA Note Technique C NT 0BMG 97-001.

Pereira A, Sundström B, 2003. Two dimensional near-field calculations of radionuclide releases from the vaults of the SFR 1 repository. SKI Report 2004:02, Statens kärnkraftinspekton (Swedish Nuclear Power Inspectorate).

Sahai N, Sverjensky D A, 1997. Evaluation of internally consistent parameters for the triple-layer model by the systematic analysis of oxide surface titration data. Geochimica et Cosmochimica Acta 61, 2801–2826.

Saufi S M, Ismail A F, 2002. Development and characterization of polyacrylonitrile (PAN) based carbon hollow fiber membrane. Songklanakarin Journal of Science and Technology 24, 843–854.

SKB, 1999. Deep repository for long-lived low- and intermediate-level waste. Preliminary safety assessment. SKB TR-99-28, Svensk Kärnbränslehantering AB.

SKB, 2001. Project SAFE. Compilation of data for radionuclide transport analysis. SKB R-01-14, Svensk Kärnbränslehantering AB.

Stone A T, Morgan J J, 1990. Kinetics of chemical transformations in the environment. In Stumm W (ed). Aquatic chemical kinetics: reaction rates of processes in natural waters. New York: Wiley, 1–42.

Stumm W, Morgan J J, 1996. Aquatic chemistry: chemical equilibria and rates in natural waters. New York: Wiley.

Surianarayanan M, Vijayaraghavan R, Raghavan K V, 1998. Spectroscopic investigations of poly-acrylonitrile thermal degradation. Journal of Polymer Science Part A: Polymer Chemistry 36, 2503–2512.

Tanaka K, 1982. Novel water-swellable fibers having a high degree of water-swellability and excellent physical properties and process for producing the same. U.S. Patent 4,366,206.

Usami T, Itoh T, Ohtani H, Tsuge S, 1990. Structural study of polyacrylonitrile fibers during oxidative thermal degradation by pyrolysis-gas chromatography, solid-state carbon-13 NMR, and Fourier-transform infrared spectroscopy. Macromolecules 23, 2460–2465.

van Loon L R, Glaus M A, 1998. Experimental and theoretical studies on alkaline degradation of cellulose and its impact on the sorption of radionuclides. PSI Report 98-07, Paul Scherrer Institut, Switzerland.