Deliverable 3.1

State-of-the-art report on cement-organic-radionuclide interactions

Work Package 3, CORI

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Executive Summary

This document presents the state-of-art on key topics addressed in CORI and provides supporting background information relevant to the specific scientific and technical context investigated in this project.

In the SOTA, a short introductory chapter summarizes the main scope and content of CORI, against which the SOTA is developed.

The degradation of selected organic materials by hydrolytic and radiolytic processes is discussed in Chapter 2. The principal organic materials present in LILW-LL waste are introduced and the main characteristics of the organic polymers studied in CORI explained. Under disposal conditions, radiation and the presence of water are the main factors relevant for polymer ageing. The degradation of polymers through radiolysis is discussed and the factors affecting the radiolytic yields for gas production explained. Radiolysis leads also to the production of non-gaseous degradation products. Some of the oxidised species generated can be dissolved in water and released when polymer waste comes into contact with water. The main steps characterizing the degradation of polymers due to the dual effect of radiolysis and hydrolysis are described by the polymer reaching equilibrium, the solubility of water-soluble species, and the hydrolysis of the polymer. The release of water-soluble degradation products depends on several controlling factors, and the organic species released by each polymer are likewise rather specific. The different materials under investigation in CORI are discussed with both mechanistic understanding and quantitative information on degradation processes being provided.

The current understanding on the behaviour of organic molecules in cement-based material is summarized in Chapter 3 focusing on the binary systems featuring organics and cement materials. The provided overview on organic molecules addresses their properties in solutions related to cementitious environments, their sorption behaviour and their diffusion behaviour. An overview of the different organic molecules potentially relevant in this context is given according to present ThermoChimie database selections. Interaction processes of organic molecules with cement materials are explained, with examples from literature mainly taken from the ISA system. Information on organics diffusion in cement materials is provided. The need of providing new data on organics retention in cement systems is emphasized, in view of the scarcity of present data, the large range of systems in terms of cement degradation states and cement formulations, as well as the complexity of organics speciation in high pH environments.

Adding further complexity and focusing on ternary systems containing radionuclides, organics and cement materials, the SOTA Chapter 4 provides an overview on the current knowledge regarding radionuclide and organic ligands interactions in cementitious environments. The main processes controlling RN migration are solubility, retention processes and physical transport. Radionuclide chemistry in cementitious environments needs to take into account the specific characteristics of speciation and solubility under alkaline conditions. This is especially relevant when considering the presence of organics materials. The radionuclide uptake in cementitious materials is summarized and references made to main publications is this field. By introducing organic ligands, the radionuclide retention on cement materials can be significantly influenced, as is explained by several examples from recent literature. A mechanistic approach to the understanding and description of retention processes in complex materials like cement needs the application of a bottom-up approach, focusing on the behaviour of the main sorbing minerals (*e.g.* C-S-H phases). This approach requires focused experiments to understand the extent of the effects of organics on RN retention, but also a thermodynamic description of the aqueous and solid species formed. After introducing main theoretical concepts and equations, the radionuclide diffusion in cementitious materials under the presence of organics is discussed. Detailed quantitative data about the diffusive transport of radionuclide-organic complexes in cementitious materials remains largely an open issue.

To provide fundamental information on the topic which may not be available with the average reader, the final Chapter 5 of the SOTA provides an introduction to fundamental cement chemistry. Different types of cement are available and the chemical properties of the cement-based materials and their mineralogy depend on the chemical composition of the cement. The compositions of the main types of cement are introduced and shown in a ternary diagram for CaO-SiO_2-Al_2O_3. Once cement is hydrated with water, solid phases including water molecules are formed, called cement hydrates. The Calcium Silicate Hydrate (C-S-H) system is discussed in more detail, based on examples from literature. Separate sub-chapters address topics related to the composition of pore solutions and the specific case of superplasticisers. The degradation of cement-based materials is explained, considering the corresponding pH decrease as a function of time and the definition of the degradation stages. The cement-based materials form a complex chemical system, which is not in equilibrium in most of the cases, especially in the context of a deep geological radioactive waste repository. The cementitious matrix is composed of several minerals, which play a role for the chemical evolution and the related radionuclide sorption processes. There is generally a good knowledge regarding the cement chemistry and a wide literature dedicated to the various cement types, which allows to characterize their chemical evolution with time and their contribution in terms of sorption.

Each sub-chapter is supported by the list of relevant key literature cited. The SOTA includes more than 150 references in total, thus providing direct references to more detailed information on the cement-organic-radionuclide interactions studied in CORI.

CORI has prepared this State-of-Art report within EURAD on cement-organic-radionuclide interactions as Deliverable D3.1. Feeding into D3.1 are Technical Reports developed on CORI at Task level, which focus on specific topics, namely

- **organic degradation by hydrolytic and radiolytic processes**
  [CNRS (**SUBATECH**)] [**Andra**],

- **organic-cement interactions**
  [KIT (**Amphos21**)] [**Andra**],

- **radionuclide-organic-cement interactions**
  [**CEA**] [**CIEMAT**], and

- **fundamental cement chemistry**
  [**Andra**] [**CEA**] [**CIEMAT**] [CNRS (**SUBATECH**)] [**KIT**] [KIT (**Amphos21**)].

D3.1 is organized according to the three RD&D Tasks defined in CORI and includes an additional chapter on fundamental cement chemistry. An introductory chapter is introducing the topics addressed in CORI, also giving information on relevance and the expected impact. All Task leaders in CORI contributed to the writing of the SOTA documents. The leading authors of the individual technical chapters are indicated.

The Deliverable is written as a consistent document covering the main aspects addressed in CORI. However, the sub-chapters were also prepared in a way so that they can be read as stand-alone documents on the respective sub-topics. This provides more flexibility in terms of integration into KM activities or Training Events in EURAD. Each section features an extended list of further literature.

This document will be updated at month 48 as *D3.2 CORI - SOTA UPDATE on cement-organic-radionuclide interactions* integrating the new findings generated in CORI.

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List of Tables

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Glossary

An	Actinide(s)
C-A-S-H	Calcium aluminium silicate hydrate
C-S-H	Calcium silicate hydrate
CAST	Carbon-14 Source Term, EC project
CEM 1-5	Cement degradation stages
DVB	Divinylbenzene
EPDM	Ethylene propylene diene monomer terpolymer
EPR	Ethylene propylene rubber copolymer
EDTA	Ethylenediaminetetraacetic acid
PHREEQC	Geochemical modelling code
GLU	Gluconate
Gy	Gray
HPC	Hardened cement paste
ILW	Intermediate level waste
S.I.	International system of units
IER	Ion exchange resins
ISA	Isosaccharinic acid
Ln	Lanthanide(s)
LET	Linear energy transfer, "stopping power"
LFER	Linear free-energy relationships
LLW/VLLW	Low-level waste / Very low-level waste
LILW-LL	Long lived low and intermediate level waste
OPC	Ordinary Portland cement
PAN	Polyacrylonitrile
PC	Polycarbonate
PE	Polyethylene
PI	Polyimide
PMMA	Polymethyl methacrylate
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PUR	Polyurethane
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
RWMD	Radioactive waste management and disposal
G	Radiolytic yield
RN	Radionuclide(s)
Eh	Redox potential
RD&D	Research development and demonstration
SCM	Supplementary cement materials
SOTA	State of art report
NEA-TDB	Thermochemical database project of the OECD-NEA
TDB	Thermodynamic database
TOC	Total organic carbon
TBP	Tributyl phosphate
WMO	Waste management organisation

1. Definition of scope and content of EURAD-CORI

The Workpackage CORI in EURAD works to improve the knowledge on the organic release issues which can accelerate the radionuclide migration in the context of the post closure phase of geological repositories for ILW and LLW/VLLW, including surface/shallow disposal. CORI objectives address topics in the context of cement-organic-radionuclide interactions. Organic materials are present in some nuclear waste and as admixtures in cement-based materials and can potentially influence the performance of a geological disposal system, especially in the context of low and intermediate level waste disposal. This potential effect of organic molecules is caused by the formation of complexes in solution with radionuclides of interest (actinides and lanthanides, but also other metal cations like Ni) which can (i) increase the radionuclide solubility and (ii) decrease the radionuclide sorption. Organic substances require increased attention since a significant quantity exists in the waste and in the cementitious materials, with a large degree of chemical diversity. Cement-based materials will be degraded with time in the context of waste disposal inducing a large range of alkaline pH conditions according to their degradation stage. Alkaline pH provides specific conditions under which the organics can degrade, which contributes to increasing their impact on repository performance. The most critical open topics and data needs required to better assess and quantify cement-organics-radionuclides interactions are reflected in the three RD&D oriented CORI Tasks.

- Organics degradation
- Organics-cement interactions
- Radionuclides-organics-cement interactions

CORI Task 2 focusses on Organics Degradation. Focus is on the characterization of soluble organic species generated by radiolytic and hydrolytic degradation of selected organics (PVC, cellulose, resins, superplasticizers). Studies also include the analysis of degradation/stability of small organic molecules such as carboxylic acids. Determination of degradation rates of polymeric materials and small molecular weights molecules are also be performed.

CORI Task 3 addresses Organic-Cement Interactions. Studies focus on investigating the mobility of selected organic molecules in cement-based materials. Mobility of organic molecules includes retention and transport properties. Organics also include small ^{14}C bearing molecules as identified in the previous EC funded project CAST. Both retention on individual cement minerals and actual cementitious systems are investigated. Analysing the fate of the organics in cementitious environments is a key requirement to understand and model the radionuclide behaviour in single and complex systems.

CORI Task 4 investigates Radionuclide-Organic-Cement Interactions. Processes of radionuclide migration are studied in the ternary system. The role of organic molecules on the transfer properties of radionuclides are investigated through retention and transport experiments, covering a range of experimental conditions (relative amounts of radionuclide–cement–organics solutions). Selected radionuclides cover a range of chemical characteristics and redox states relevant for the expected conditions in L/ILW disposal.

Predicting and assessing radionuclide transport is a key topic in nuclear waste disposal. For radionuclide behaviour in cementitious environments where large inventories of organic materials may be present, CORI aims to significantly improve the present knowledge. An improved quantification of radionuclide solubility and retention phenomena in cementitious environments can provide important input into predicting radionuclide transport. In view of this general motivation in CORI, specific benefits in terms of impacting implementation or safety are described below.

Regarding RWMD implementation needs:

Issues of interest at the repository scale are identified:

- Improved scientific basis for the Safety Case for L/ILW waste repositories featuring relevant organics content.
- Co-storage of waste: support decisions regarding the question whether or not a mix of various wastes (organics, soluble salts, exothermic waste) can be foreseen.
- Optimization of vault design: limitations of interactions between the vaults regarding their content. CORI will provide information on the organic plume by characterizing the transfer behavior in cement-based materials.
- Optimization of concrete formulations as regards the potential effect of superplasticizers on radionuclide transfer properties.

Regarding safety:

- Characterizing the effect of the organic plume on the behavior of radionuclides in terms of:
  - solubility (limitation of solubility increase),
  - sorption (limitation of retention decrease) in terms of K_d values.
  - retention of potentially ^{14}C-bearing organic molecules (determined in CAST project) in cementitious environments in the case of specific waste.
- This projects aims to:
  - reduce the uncertainties on the current knowledge (mainly K_d values),
  - improve the knowledge on the known organic molecules present in degradation solutions (not considered so far) with their complexing properties: better definition of the organic inventory regarding the waste and the concrete vault (geological and surface repositories).

CORI has established a focused Workplan based on the three identified RD&D Tasks given above. In order to perform cutting-edge research and make best use of available resources, it was essential to focus and not to investigate a too broad set of topics. It was therefore decided that CORI will <u>NOT</u> study several other related topics like microbial degradation of organics, bitumised waste, iron corrosion in cementitious environments, work related to the conditioning of waste in cement materials or studies on natural organics present in certain host-rocks. Studies primarily targeting to derive new thermodynamic data for databases were not included, although it is acknowledged that complete and reliable thermodynamic data and databases are essential. The limited modelling performed within CORI is necessary to analyse and systematize the new experimental data and findings from CORI in the RD&D Tasks. CORI does not perform any PA related modelling studies. These limitations regarding the scope of CORI is also reflected in the SOTA document prepared, which focusses on the main topics addressed in CORI and thus cannot at all be considered a comprehensive exhaustive survey of all relevant topics.

2. Organic degradation by hydrolytic and radiolytic processes

*Authors: Denise Ricard [**Andra**] and Johan Vandenborre [CNRS **(SUBATECH)**]*

2.1 Organic waste

Organic materials are present in various forms in low or intermediate level wastes: as paper, gloves, over-clothing, flasks, filters, seals, cables, ion exchange resins, *etc*.. Organic materials can also be part of the cement matrix, like in the form of superplasticizers. The radioactivity of organic waste is due mostly to the presence of contamination on the surface of the waste by fission products, activation products and/or actinides. Principal polymers present in long-lived low and intermediate level waste (LILW-LL) are summarized in *TABLE* 2-1.

TABLE 2-1*: Principal organic materials present in LILW-LL waste.*

Chloropolymers	***Polyolefins and associated copolymers***
Polyvinyl chloride *(PVC)*	Polyethylene *(PE)*
Polychloroprene *(Neoprene®)*	Polypropylene *(PP)*
Chlorosulfonated polyethylene *(Hypalon®)*	Ethylene propylene rubber (*EPR*) copolymer
Fluoropolymers	Ethylene propylene diene monomer *(EPDM)* terpolymer
Polytetrafluoroethylene *(PTFE, Teflon®)*	***Miscellaneous***
Polyvinylidene fluoride *(PVDF)*	Polycarbonate *(PC)*
Vinylidene fluoride-hexafluoropropylene copolymer *(Viton®)*	Polyurethane *(PUR)*
Polyacrylate	Polyamides *(Nylon®)*
Polymethyl methacrylate *(PMMA)*	Polyimide *(PI)*
Polyacrylonitrile *(PAN)*	Cellulose
Ion exchange resins (IER)	Epoxy resin
Styrene-divinylbenzene copolymer	Silicone
Polyacrylonitrile based resins	Polybutadiene
	Superplasticizers

The percentages by mass of the various organic materials present in the French ILW waste are presented in *FIGURE* 2-1. The total mass of polymer ILW waste is listed as 1.600 tonnes (PIGD, 2014). *FIGURE* 2-2 and *TABLE* 2-2 show the organic waste inventories for ONDRAF/NIRAS and SKB, respectively.

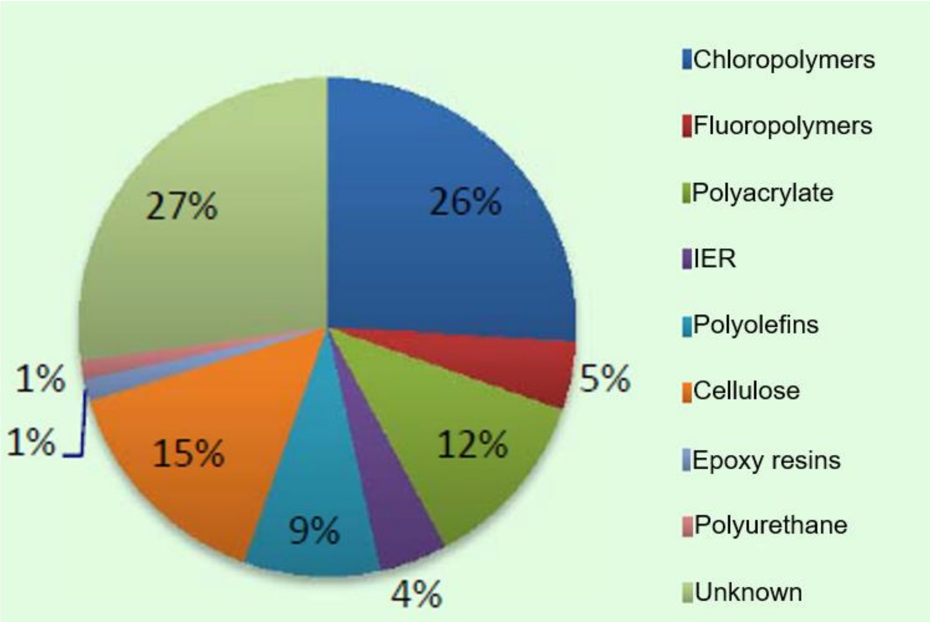


FIGURE 2-1: *Distribution of organic materials present in the French ILW waste in percentage by mass (information provided by Andra).*

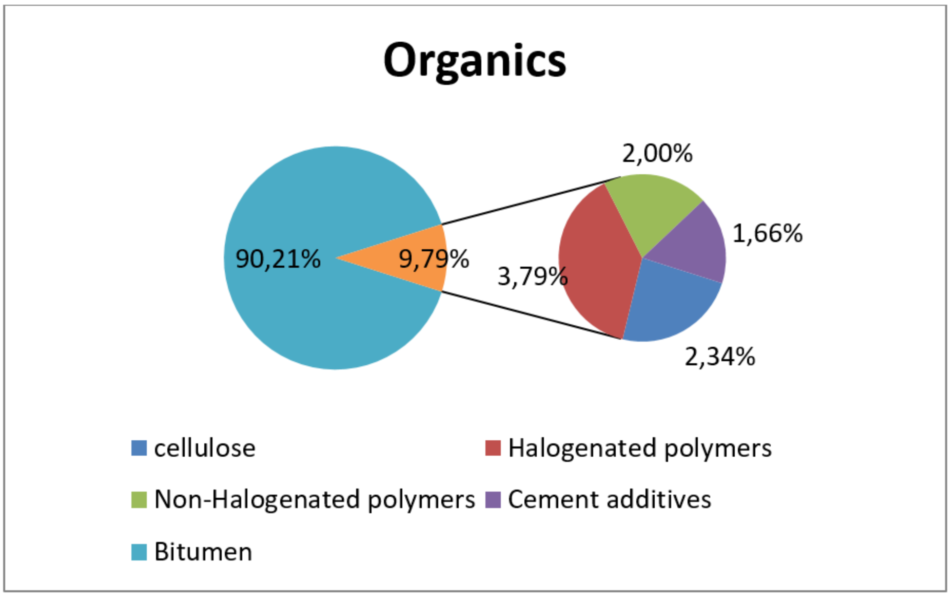


FIGURE 2-2: *ONDRAF/NIRAS organic inventory (information provided by ONDRAF/NIRAS).*

***TABLE 2-2**: Bulk amount of organic materials in SKB inventory (information provided by SKB).*

Bulk material	In SFR [t]	Source	Interest
Ash	700	Pyrolysed legacy waste	
Cellulose	700	Various, e.g. concrete	Microbes, gas production. ISA
Ion-exchange resin	11 700	Treatment of active water	
Filter aids	1 300	With ion-exchanger	Degrades to complexing agents
Evaporator concentrate	400	Wash water	
Rubber and plastics	1 400	Various, e.g. packaging	
Sludge	300	Decont., filter aids, etc.	
Sand and soil	6 200	Mostly inorganic	
"Other organic"	1 200	Catch-all. Previously included some above materials	Microbes, gas production
Bitumen	2 900	Solidification of fluid waste	Assumed low porosity & diffusivity. Inert (?)

2.2 Organic materials selected in EURAD-CORI

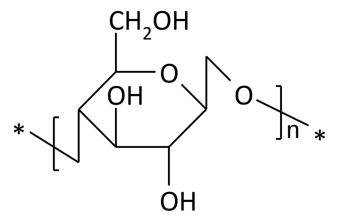
The following organic materials were selected to be studied in Task 2 of EURAD-CORI: polyvinyl chloride (PVC), cellulose, ion exchange resins (IER) and superplasticizers. These organics represent the most abundant/important materials in the WMO's inventories.

Polymers used in the nuclear sector are industrial materials used in equipment such as electric cable sheathing, seals, and the gloves, sleeves or panes of glove boxes. The characteristics of commercial materials based on cellulose, PVC and IER frequently used in the nuclear sector are discussed in the following.

Superplasticizers will not be considered in the present SOTA document .The characteristics and results related to the behaviour of these materials will be included in the last version of the SOTA that will updated by the end of the project.

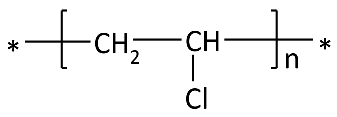
2.2.1 Cellulose

Cellulose is a polymer made up of D-glucose groups with the chemical formula presented below. This material is historically used in the nuclear industry as tissue for smear-testing potentially radioactive particles. However, in some countries, like Belgium and Sweden, other materials have replaced the cellulose in order to decrease their amounts in disposal. Cellulose can also be found in paper textile, filters, wood and cardboard materials.



2.2.2 Polyvinyl chloride (PVC)

Polyvinyl chloride (PVC) is a chloropolymer with the chemical formula presented below.



This material is primarily present in the waste as bags or glove box sleeves, but also as thicker material such as used in filter casings. For ventilation filter seals, an example of the composition is:

- 27 % of pure PVC (50/50 mixture by mass of Solvin® 266 SF and Solvin® 372 LD);
- 14 % $CaCO_3$;
- 2 to 3 % $Ca(OH)_2$;
- 30 % plasticisers (di-n-butyl phthalate, diisononyl phthalate, 2-ethylhexyl diphenyl phosphate);
- 24 % inorganic fire retardants ($Al(OH)_3$ and Sb_2O_3).

For bags or glove box sleeves, an example of the composition is:

- 63 % resin (PVC K70 and PVC K75);
- 31 % plasticisers (di-isononyl phthalate (DINP);
- 1.4% heat stabilisers (organic derivatives of Ca/Zn metals);
- 2.25% of additives (stearic acid, calcium stearate, talc powder).

2.2.3 Ion Exchange Resins (IER)

Ion exchange resins (IER) are solids that have the capacity to exchange the ions they contain with other ions from a solution, often with specific selectivity. IERs are primarily used by the nuclear industry for treating and decontaminating the water used in spent fuel unloading and storage pools. IERs are made up of:

- an organic polymer skeleton (with a three-dimensional network);
- functional groups fixed to the polymer skeleton that provide the ion exchange function within the material (cationic or anionic).

There are several types of polymer skeletons, including for example:

- polystyrene skeleton: this is obtained by polymerisation of styrene followed by cross-linking using divinylbenzene (DVB), see *FIGURE* 2-3.

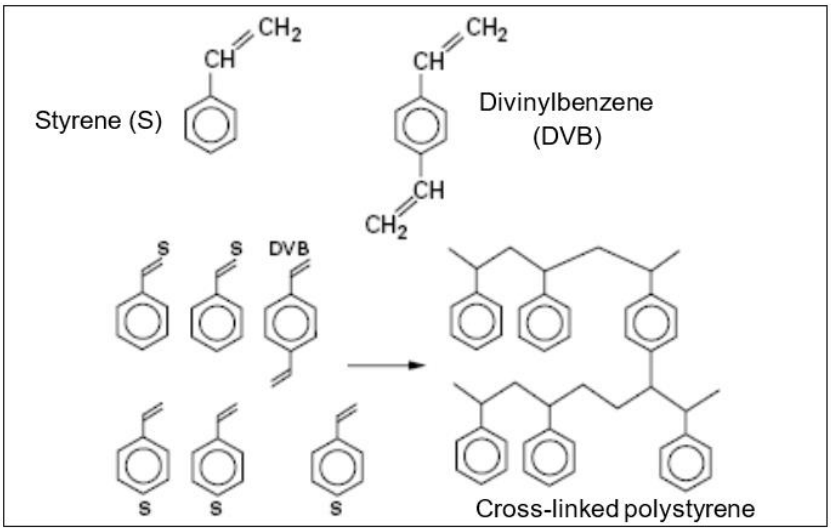


***FIGURE 2-3**: Formation of a polystyrene skeleton (De Dardel, 1998).*

- polyacrylic skeleton: obtained by polymerisation of a methacrylate and cross-linking with divinylbenzene (see *FIGURE 2-4*).

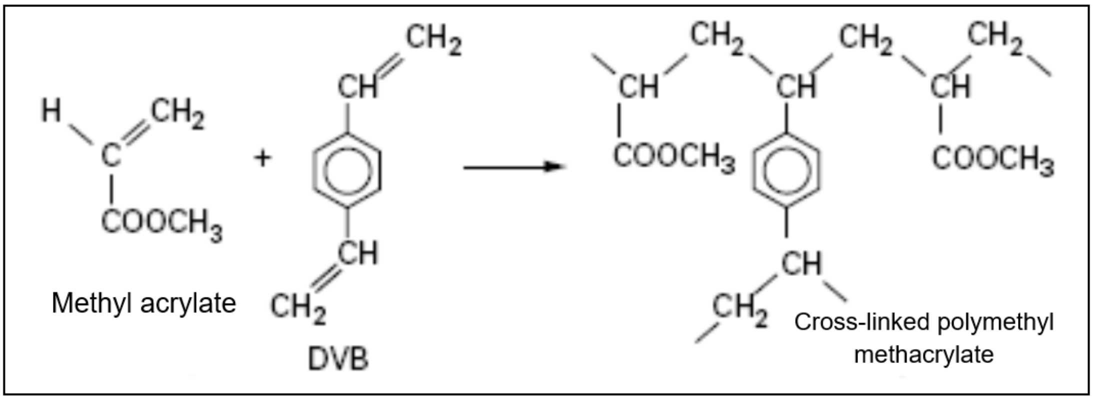


***FIGURE 2-4**: Formation of a polyacrylic skeleton (De Dardel, 1998).*

2.3 Ageing of polymers

Under disposal conditions, radiation and the presence of water are the main factors of polymer ageing. These two processes of ageing or degradation are described below.

2.3.1 Degradation of polymers through radiolysis

In polymers, molecular changes induced by irradiation can be of various kinds (O'Donnell, 1989), including:

- chain cross-links and splits;
- release of volatile compounds (hydrogen H_2, carbon oxides CO and CO_2, molecules with low molecular mass (*e.g.* methane CH_4, *etc*.);
- formation of unsaturated species ("double bonds");
- formation of non-gaseous degradation products (*i.e.* molecules with a low molecular mass (alcohols, carboxylic acids, *etc*.).

2.3.2 Production of gas through radiolysis

Production of gas through the radiolysis of organic material is a process that occurs already from the manufacturing of the packages. It diminishes over time due to the decreasing radioactive decay and hence activity of the waste, and the changes in the materials under radiation.

The main gases produced by radiolysis are hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), and methane (CH_4). If the polymer is chlorinated or fluorinated, hydrogen chloride (HCl) or hydrogen fluoride (HF) can also form.

Hydrogen is produced by the majority of the polymers to be considered in disposal, while CO and CO_2 are mainly formed under oxidising conditions. If C-O or O-O-O bonds are present within the structure of polymers, production of CO and CO_2 may also occur under anaerobic conditions (for example cellulose or polyurethane). As specified above, hydrogen chloride is produced from chlorinated organic materials. These are the most abundant polymers in the waste considered for deep geological disposal. In some packages, the presence of fluorinated polymers can lead to the formation of hydrogen fluoride. It is essential to quantify gaseous hydrogen production because it is a flammable gas that may even cause explosions in the presence of air (O_2). Hydrogen chloride and hydrogen fluoride need to be specifically quantified due to their corrosive action on steels. These corrosive gases can thus have consequences on the stability of primary packages, especially during storage and disposal phases.

The production of gases from a waste package containing organic polymers is calculated by considering:

- the nature and activity of the radionuclides associated with the organic waste, and
- the gas production radiolytic yield values for each organic material present in the package.

Radiolytic yield is defined as the concentration of the radiolytic species formed in relation to the quantity of energy deposited by ionising radiation. The radiolytic yield is denoted G and expressed, in S.I. units, in $mol \cdot J^{-1}$. For polymer irradiation, G can represent the yield for the creation of a new group in the polymer chain, the yield for the release generation of a gas or small molecule, or the yield for destruction of a group initially present in the irradiated compound.

In the following paragraphs, the discussion will focus mainly on the radiolytic gas generation.

2.3.3 Variability of radiolytic yields for gas production

Various parameters can affect the radiolytic yield values for gas production, such as:

- the effect of additives / the formula;
- the effect of LET [1] (Linear Energy Transfer);
- the effect of the dose [2];
- the effect of the relative humidity;
- the effect of the temperature.

Detailed results on the effect of these parameters are given in document (EURAD-CORI, MS17).

Influence of the formulation

In industrial polymers, the presence of fillers and additives can influence gas production. Since there is generally a low quantity of stabilisers, their effect can only be seen at low radiation doses.

Industrial halogenated polymers contain additives like calcium fillers $Ca(OH)_2$ or $CaCO_3$ which offer the advantage of capturing corrosive gases like HCl. For some industrial PVC, the HCl can be completely captured by additives while for others the HCl capture will only be partial.

Influence of LET

LET (linear energy transfer) represents the deposit of energy transferred by the particle encountering the environment per unit of length in the material considered. This parameter is characteristic of ionising radiation. The β particles and γ radiation on the one hand, and the α particles and the neutrons on the other differ by their energy deposit induced in the irradiated materials. The former induce low LET, while the latter lead to higher LETs (difference of a factor ~1000).

FIGURE 2-5 shows the variation in the H_2 formation yield with LET for several polymers: polyethylene, polypropylene, poly(methyl methacrylate) and polystyrene (Chang & Laverne, 2000). Increasing the LET from 0.2 eV/nm (associated to γ radiation) to 800 eV/nm leads to an increase of G_{H2}. However, this increase also depends on the chemical composition of the polymers: a factor of about 2 is observed between lowest and higher G_{H2} values for saturated polyolefins, (polyethylene or polypropylene type), about 10 for poly(methyl methacrylate) and around 30 for polystyrene.

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[1] LET refers to the quantity of energy transferred by the particle to the material per unit of distance covered in the material.

[2] Dose refers to the energy deposited per target unit of mass. This is normally expressed in Gray (Gy), where 1 Gy = 1 J·kg^{-1}.

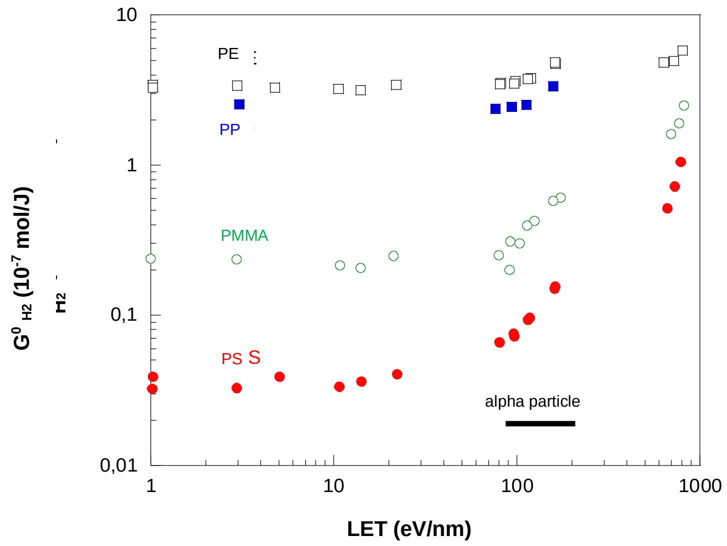

FIGURE 2-5. Variation of H_2 production yields as function of LET for polyethylene (PE), polypropylene (PP), poly(methyl methacrylate) (PMMA) and polystyrene (PS) (Chang & Laverne, 2000).

The observed different behaviour verified according to the polymer composition can be interpreted as follows:

- For saturated polyolefins, the yield is virtually independent of LET. H_2 is formed very quickly and is insensitive to the density of ionisation and excitation in the lobes. This is attributed to the reactivity of H° radicals.
- For polymers containing unsaturated groups, G_{H2} is practically constant for low LET values and then increases from a threshold LET value. However, these materials benefit from a protective effect associated with the presence of unsaturated groups. Increased LET leads to densification of energy deposition which seems to have the effect of reducing this protection.

In summary, the effects of LET are more important for unsaturated polymers and, in some conditions, for halogenated polymers. Oxidation also seems to depend significantly on the type of ionising particles.

Influence of the dose

The main effect of the dose is to modify the chemical composition of the polymer. The structure of the material changes during irradiation, leading to variations in the way in which energy is deposited in the medium.

The instantaneous radiolytic yield for H_2 formation for polyethylene (PE) has been described by (Venture *et al.*, 2016) for doses up to 12 MGy. For these studies, PE was subjected to irradiation under inert conditions with 1 MeV electrons and ^{20}Ne high-energy ions. The results show that G_{H2} drops with the dose, for both types of irradiation, and that these values tend to stabilise at high doses. High-dose G_{H2} values are around 2×10^{-7} mol·J^{-1} and 3×10^{-7} mol·J^{-1} for electron and ^{20}Ne ion irradiations, respectively. These values correspond, respectively, to ≈ 50 % and ≈ 65 % of the G_{H2} values of PE at the initial dose ($G_{0,H2}$).

For pure PVC and industrial PVC, a decrease in the yield of H_2 and HCl with the dose was recorded (Colombani; 2007).

In conclusion, it is evident that the dose influences the yields of gas formation. The instantaneous yields G_{H2} and G_{HCl} decrease with the dose. For H_2, this decrease is mainly due to the formation of unsaturated defects, whereas for HCl the mechanism is via dehydrochlorination of the material. For the other gases and particularly for gases produced by the oxidation of materials (CO, CO_2), the yields can increase with the dose, being related to the accumulation of oxidation products.

Influence of relative humidity

Few studies have been conducted regarding the effect of humidity on the degradation of polymers used in the nuclear industry under irradiation.

A recent study was carried out by CEA/ORANO on a formulated PVC at a high dose rate (3-4 $kGy \cdot h^{-1}$), under aerobic conditions and integrated doses from 0.1 to 4 MGy. The difference of radiolytic yields of $HCl_{trapped}$ for PVC irradiated under low relative humidity conditions (of around 10%) and high relative humidity (74%), is less than 10%. For H_2 production, $G_{H2}^{\beta\gamma}$ is equal to 0.95 molecules/100 eV for 10% of relative humidity and equal to 1.07 molecules/100 eV for 74% of relative humidity conditions (Andra).

In summary, the yields of HCl and H_2 formation from industrial PVC are influenced little by relative humidity.

For cellulose, A.R. Kazanjian (Kazanjian, 1976) compared the gas emission of a dry cellulose and a mixture containing 40% cellulose and 60% water by weight. The apparent yields measured are higher for dry cellulose. This result is expected since the yield of H_2 formation by the radiolysis of water is lower than the yield of cellulose. It seems that the effect of the presence of water is therefore limited.

Although the effect of relative humidity has not been studied extensively, the available data suggests that this factor does not play a significant role in the radiolysis of organic polymers.

Influence of temperature

The effect of temperature on the production of gas was studied on polyethylene by CEA/ORANO. Series of irradiations were carried out on a polyethylene under helium and under air at ambient temperature and at 120°C. An increase in H_2 production was observed at 120°C. This increase is much more marked in the presence of oxygen (radiolytic yield of H_2 is 17.1×10^{-7} $mol \cdot J^{-1}$ under air, and 5.5×10^{-7} $mol \cdot J^{-1}$ under helium) (Andra).

The effect of temperature on the production of gas from PVC under radiolytic contitions was studied for pure and industrial polymers. Boughattas (Boughattas, 2014) studied, for example, the effect of temperature on the radiolytic yields of HCl, H_2 and benzene formation, measured during irradiation campaigns on pure PVC and industrial PVC under helium and under air at different temperatures (80°C, 100°C, 120°C and 150°C). Results indicate that the temperature has a relatively small effect on the production of H_2 for pure or commercial PVC. On the other hand, the radiolylic yield G_{HCl} for pure PVC increases with temperature. The generation of HCl under air is systematically higher than that recorded under inert conditions.

2.3.4 Summary of radiolytic yield values

TABLE 2-3 summarises the values of maximum radiolytic yields obtained for the polymers considered in Task 2 of EURAD-CORI. The values available for the other organic materials present in ILW waste packages are available in the document (Eurad-CORI Milestone 17). Most of these values were obtained by the CEA/ORANO from γ irradiation and heavy ion irradiation at ambient temperature and under homogeneous oxidation conditions (Andra). Some of the values given apply to industrial polymers present in packages of waste (gloves, cables, filters, *etc*.). The rest apply to pure polymers with no fillers or additives. *TABLE* 2-3 specifies whether the values of radiolytic yields reported are taken from the literature rather than the work of the CEA.

For some polymers, the only available values of radiolytic yields refer to γ radiation. Estimates are therefore used to establish values of α radiolytic yields. Therefore, two approximations concerning the radiolytic yields of H_2 formation under α radiolysis can be made if data is unavailable. Either the radiolytic yield of formation of this gas is taken as equal to that from polyethylene, or it is taken as equal to 4.5 times that of the material in question under γ radiolysis. The first approximation is used when the material is aliphatic. The second approximation is used when the material contains unsaturated groups. Furthermore, for the other gases (CO, CO_2, CH_4, HCl, HF), it is always considered that G^{α} is equivalent to $G^{\beta\gamma}$.

The values of radiolytic yields of CO_2 and CO production are particularly high. The production of these gases depends on the oxidation rate of the polymer and is therefore highly dependent on the conditions under which the material is exposed to oxidation and radiation. In the case of irradiation carried out at the CEA, sufficiently thin polymers were generally used so that oxidation occurred evenly across the entire thickness under irradiation. However, in ILW packages containing polymer organic materials, organic materials are thicker as the waste is compacted or packaged in bulk in the packages. Oxidation of the various organic materials will therefore not necessarily occur evenly within the materials. The maximum values of radiolytic yields of CO_2 and CO are thus very conservative. For some of the polymers, greater quantities of these two gases will be produced during the repository operating phase under oxic conditions.

***TABLE 2-3**: Maximum gas radiolytic yields for several polymers present in ILW waste packages (values were obtained by the CEA/Orano, unless otherwise specified)* (Andra).

Polymer	Radiolylic yield ($\times10^{-7}$ mol·J^{-1})	Material/ Dose
Polyethylene (PE)	$G^{\beta\gamma}_{0,\,H_2} = 3.4$ $G^{\beta\gamma}_{CO_2} = 1.8$ $G^{\beta\gamma}_{0,\,CO} = 0.41$ $G^{\beta\gamma}_{0,\,CH_4} = 0.026$	Pure PE under air, G at zero dose
	$G^{\alpha}_{0,\,H_2} = 3.9$ $G^{\alpha}_{0,\,CO_2} = 3.6$ $G^{\alpha}_{0,\,CO} = 1.2$ $G^{\alpha}_{0,\,CH_4} = 0.162$	Pure EPDM under air, G at zero dose Pure EPDM under air, G at 8 MGy Pure PP under air, G at zero dose Pure PP under air, G at zero dose
Cellulose	$G^{\beta\gamma}_{0,\,H_2} = 2.5$	Industrial Cotton under air, G at zero dose

Polymer	Radiolytic yield ($\times 10^{-7}$ mol·J^{-1})	Material/ Dose
	$G^{\beta\gamma}_{0,\,CO_2} = 2.3$ $G^{\beta\gamma}_{0,\,CO} = 1.6$ $G^{\beta\gamma}_{0,\,CH_4} = 0.01$	
	$G^{\alpha}_{0,\,H_2} = 2.5$ $G^{\alpha}_{CO_2} = 1.7$ $G^{\alpha}_{CO} = 0.84$ $G^{\alpha}_{CH_4} = 0.005$	$G^{\alpha}_{0,\,H_2} = G^{\beta\gamma}_{0,\,H_2}$ industrial cotton under air, G at zero dose Industrial Cotton under air, G at 3.9 MGy Industrial Cotton under air, G at 3.9 MGy Industrial Cotton under air, G at 7.1 MGy
Polyacrylonitrile	$G^{\beta\gamma}_{0,\,H_2} = 0.25$ $G^{\beta\gamma}_{0,\,HCN} = 0.04$	G at zero dose (Burlant & Taylor, 1955)
	$G^{\alpha}_{0,\,H_2} = 1.1$	$G^{\alpha}_{0,\,H_2} = 4.5 \times G^{\beta\gamma}_{0,\,H_2}$ (ratio observed for pure polystyrene at zero dose (Chang & Laverne, 2000))
IER	$G^{\beta\gamma}_{H_2} = 1.2$ $G^{\beta\gamma}_{CO_2} = 8.1$	IER anionic Amberlite® IRA 400 OH under air, G at 0,5 MGy IER (75% cationic, 25% anionic) Microionex® MB400 HOH under air, G at 0.5 MGy
	$G^{\alpha}_{H_2} = 3.9$	Polyethylene value (EPDM under air, G at zero dose)
Polyvinyl chloride (PVC)	$G^{\beta\gamma}_{0,\,H_2} = 0.31$ $G^{\beta\gamma}_{CO_2} = 4.2$ $G^{\beta\gamma}_{CO} = 1.0$ $G^{\beta\gamma}_{CH_4} = 0.071$ $G^{\beta\gamma}_{HCl} = 6.4$	Industrial PVC (Plastunion) under air, G at zero dose Industrial PVC (Plastunion) under air, G at 6 MGy Industrial PVC (Plastunion) under air, G at 10 MGy Industrial PVC (Plastunion) under air, G at 2 MGy Industrial PVC (Plastunion) under air, G at 10 MGy
	$G^{\alpha}_{0,\,H_2} = 0.62$ $G^{\alpha}_{CO_2} = 2.1$ $G^{\alpha}_{CO} = 1.2$ $G^{\alpha}_{CH_4} = 0.081$ $G^{\alpha}_{HCl} = 3.2$	Industrial PVC (Plastunion) under air, G at zero dose Industrial PVC (Plastunion) under air, G at 7.4 MGy Industrial PVC (Plastunion) under air, G at 7.4 MGy Industrial PVC (Plastunion) under air, G at 3.8 MGy

2.3.5 Gas production calculation method

The gas production rate at each instant "t" can be calculated using the following formula:

$$d_x = A_x \sum_i F^i \frac{1}{100} \left(e_{x,\alpha} \times G_i^{\alpha} + e_{x,\beta\gamma} \times G_i^{\beta,\gamma}\right) \qquad \text{(eq. 2-1)}$$

where:

- A_x: activity of a radionuclide X at the time t considered;
- d_x: gas production rate, in molecules per second, associated with radionuclide X;
- F^i: mass fraction of the "radiolysable" material i in the package. This mass fraction is given considering the mass of packaged waste and that of the packaging matrix (therefore excluding the container);
- $e_{x,\alpha}$, $e_{x,\beta\gamma}$: energy deposited by α or β/γ radiation in the package per 1 Bq by radionuclide X in eV/disintegration. The values of energy deposited for each radionuclide are taken from the literature;
- G_i^{α}, $G_i^{\beta,\gamma}$: radiolytic yield of radiolysable material i under α or β/γ irradiation in molecules/100 eV. These values of yields are considered to be constant over time.

Following this method, all energy from disintegration is assumed to dissipate evenly in the waste and matrix mass. This assumption is conservative for γ rays, which have a longer path than the average dimensions of the waste. This means that the γ irradiation from adjacent packages in the waste cell is effectively taken into account. This assumption is also conservative with respect to the estimate of gas production associated with α radiation. It does not take into account self-absorption phenomena for α particle radiation or the fact that the energy deposited by α particles varies across the thickness of the material.

2.4 Degradation of polymers - dual effect of radiolysis + hydrolysis

When ionising radiation interacts with polymers, non-gaseous radiolytic degradation products are produced. Some of the products generated by the radio-oxidation of the material are low molar mass oxidised species, such as alcohols, ketones or esters. These oxidised species can be dissolved in water and released when polymer waste comes into contact with water. These organic compounds can alter the mobility of radionuclides and potentially increase their migration away from the disposal site, either because of an increase in their solubility or because of a change in their retention by the different engineered barriers.

The pH values and the chemical composition of water in contact with ILW packages containing organic materials are directly connected to the physical and chemical changes to the cement-based materials that make up the disposal packages and structures of ILW disposal cells. In most of the currently designed disposal facilities, the leaching solution is expected to be cementitious water with a pH between 10.5 and 13.5. The phenomena that occur when the radiation-degraded polymer and cementitious leaching solution come into contact are summarized as follows, and described in more detail in the subsequent sections:

- the polymer in solution reaches equilibrium with the aqueous phase (water diffusion inside the polymer and solubilisation of soluble species), mainly influenced by the pH of the solution;
- diffusion of the water-soluble species which formed during the polymer irradiation, the process depending on the contacting solution and nature of the compounds formed under radiation;

- hydrolysis of the oxidised polymer.

These phenomena can occur at different time scales depending on the diffusion phenomena, the nature of the irradiated polymer (little oxidised, cross-linked, *etc*.), and the reactivity of the species in water.

2.4.1 The polymer reaching equilibrium

Thermodynamic equilibrium of the polymer with the aqueous solution requires permeation of water into the polymer. This depends on the composition of the polymer. The more the polymer contains polar groups, the more quickly water will permeate. A polymer that is hydrophobic when non-irradiated can become highly hydrophilic after oxidation under irradiation, as the formation of oxidised groups such as ketones, alcohols, carboxylic acids will facilitate the permeation of water. In contrast, polymer cross-linking will make it more impermeable to water.

2.4.2 Solubility of water-soluble species

After the water/polymer system has reached equilibrium, the water-soluble degradation products dissolve. Solubility depends on the following factors:

- the aliphatic chain length;
- polarity;
- the geometry of molecules;
- pH;
- the presence of metal ions or salts.

As a general chemical rule, the longer the carbonated aliphatic chain length, the lower the solubility of the compound in water. Solubility also depends on the dipole moment of the molecule that arises from bond polarity and geometry of the molecule. A dipole exists when a molecule has areas of asymmetrical positive and negative charge. The polarity of a bond is associated to the electronegativity difference between two atoms of a bond. The atom with larger electronegativity will have more pull for the bonded electrons than the atom with smaller electronegativity; the greater the difference in electronegativity, the larger the dipole. In a diatomic molecule (X_2 or XY), there is only one bond, and the polarity of that bond determines the polarity of the molecule. When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged so that their bond moments cancel (vector sum equals zero), the molecule is nonpolar.

The main chemical functions of organic compounds can therefore be classified according to their polarity. The following order is obtained, from the most polar function to the least polar function:

amide > carboxylic acid > alcohol > ketone ~ aldehyde > amine > ester > ether > alkane.

Since water is a polar solvent, amides, carboxylic acids and alcohols are the compounds that will be mostly solubilised in the aqueous phase. Furthermore, the more polar chemical functions there are, the more solubility is favoured. In addition, the geometry of the compound influences the solubility of the compound. A non-linear geometry favours the solubility of the compound because branching lowers intermolecular forces and decreases intermolecular attraction. Finally, the solubility of the compound depends on the ionic strength and pH of the aqueous solution. Carboxylic acids and alcohols can be in protonated or non-protonated form. Their concentration in a solution depends on its pH and their acidity constant.

The pH of the solution can also alter the solubility of compounds. The ionised (*i.e*. deprotonated) compound is easier to solubilise in water. The solubility of acids therefore increases with the pH. In the ILW repository, the water in contact with the packages will generally be cementitious water with a pH between 10.5 and 13.5. The solubilisation of acids under these conditions will be greater than in pure water. Finally, the presence of metal ions or alkalis generally increases the solubility of species by forming soluble complexes.

The diffusion of water-soluble compounds depends on temperature, as well as the steric bulk of the compound and of the solute concentration to solubilise. Therefore, the higher the temperature, the greater the diffusion coefficient. Similarly, the more the solute concentration decreases, the greater the diffusion coefficient.

2.4.3 Hydrolysis of the polymer

Independent of the previous steps, the polymer hydrolyses in contact with water. As it diffuses in the material, water reacts with the chemical functions of the polymer and can cause additional degradation. This hydrolysis mainly depends on the functional groups carried by the polymer and the pH of the aqueous solution. Furthermore, the more water-permeable the material, the greater the hydrolysis of the polymer.

The hydrolysis of degraded polymers is therefore far from negligible in cementitious water. For some materials such as polyester-based polymers, the contribution of basic hydrolysis to the degradation of the material is more significant than radiolysis.

2.5 Identification and release of water-soluble molecules

The chemical characteristics and quantities of water-soluble molecules released by organic materials in the repository depend on the nature of polymers present within the waste packages, as well as the conditions under which materials were exposed to ionising radiation and their accessibility to water from the geological medium.

2.5.1 Variability of the release of water-soluble degradation products

Several factors can influence the release of water-soluble degradation products such as:

- the irradiation conditions: dose and LET that can influence the oxidation rate of the material;
- the leaching solution: pH, presence of counter-ions, *etc*.;
- the formulation of the material: nature of the polymer, composition of the material (pure or industrial), presence of additives, presence of mineral fillers which can trap HCl, *etc*..

Detailed results on the effect of these parameters are given in document (EURAD-CORI Milestone 17).

Influence of irradiation conditions

The effect of the type of irradiation on the release of soluble species was evaluated by CEA/ORANO for various polyurethanes (PUR Estane, PUR Mapa, PUR Piercan, PUR Manche), for the PVC representative of glove box bags or sleeves (Plastunion PVC), Hypalon®, Neoprene® and PC (Lexan). These polymers were irradiated at 4 MGy and then leached for one month in pure water. The following carboxylic acids were investigated in the leaching solution: formic, glutaric, acetic, phthalic acids.

The highest concentrations of organic acids are obtained for polymers irradiated under γ rays, as the oxidation rate is greater under this type of radiation. Only polycarbonate produces more acids when it is irradiated with heavy ions than under γ radiation. This behaviour can be associated with the presence of aromatic groups that are sensitive to a stopping power effect (Andra).

Influence of LET (stopping power)

The effect of LET or stopping power on the nature and quantity of water-soluble degradation products released in a solution was evaluated by CEA/ORANO for the following polymers: EPDM, PP, PVC and PUR. Irradiation was carried out using ^{36}S and ^{22}Ne light ions of energy equal to approximately 11.5 $MeV \cdot A^{-1}$. The concentrations of carboxylic acids measured are of the same order of magnitude regardless of the LET studied, ranging between 15 and 4 $MeV \cdot mg^{-1} \cdot cm^{-2}$ (Andra).

Influence of dose

The effect of the dose was studied by CEA/ORANO for certain polymers (PUR, EPR, PVC) irradiated under γ rays at dose rate of 0.7 $kGy \cdot h^{-1}$ and at doses of 6 and 10 MGy. Irradiation was followed by leaching in cementitious water (pH 13.2). The following carboxylic acids were investigated in the leaching solution: formic, oxalic, glutaric, acetic, adipic acids and phthalic acid for industrial PVC. The release of phthalic acid observed in the case of industrial PVC is associated with leaching of phthalate, present in this medium as a plasticiser.

The total quantity of organic carbon TOC, and thus the water-soluble degradation product concentration is similar for the two doses of radiation. From 6 MGy, the release of certain water-soluble degradation products tends to reach saturation (Andra).

It is currently impossible to establish an exhaustive list of all the compounds formed under irradiation of carbon chains and heterochains polymers containing oxygen. The majority of compounds identified are alcohols and carboxylic acids. The carboxylic acids are of various types and can be grouped into families:

- monoacids, which come from a single chain break: acetic acid and formic acid;
- diacids, which come from two chain breaks: glutaric acid and adipic acid;
- triacids, which can come from bridging between a diacid and monoacid: carballylic acid;
- α-hydroxy acids: lactic acid;
- keto acids: acetoacetic acid;
- hydroxy diacids: malic acid;
- monounsaturated acids: fumaric acid;
- aromatic acids: phthalic acid and benzoic acid.

In conclusion: the water-soluble degradation products generated by the degradation of organic polymers under radiation are mainly carboxylic acids and alcohols. Among the carboxylic acids, several families of compounds have been identified (monoacids, diacids, keto acids, aromatic acids, *etc*.). At a high dose, the release of certain water-soluble degradation products tends to reach a saturation peak.

Influence of the leaching solution

The chemistry of the contacting leaching solution is an important factor influencing the release of water-soluble degradation products. In cementitious water, the main release phenomenon for water-soluble degradation products is basic hydrolysis. The release therefore depends on the phenomenon of basic hydrolysis, whose speed depends on the composition of the degraded polymer.

The polymer leaching protocol can also play a role in the release of water-soluble products. Two types of basic water leaching protocols have been studied by Fromentin (Fromentin, 2017) during polyurethane leaching: (i) leaching with pH adjustment and (i) leaching with solution renewal. The results obtained in the work indicated that losses of mass and TOC values are higher for leaching with solution renewal as the reaction is forced towards degradation.

In conclusion, the main leaching solution parameters affecting the release of water-soluble degradation products and the associated effects are as follows:

- basic pH influences the solubilisation of ionic carboxylate species and generates basic hydrolysis of the material, which produces additional degradation of the material by splitting the chains;
- presence of counter-ions that stabilises the ionic species;
- presence of cations like K^+, Ca^{2+}, *etc*. that can form complexes with the water-soluble degradation products and whose stability will depend on the presence and concentration of metal ions (competition reactions);
- solution renewal that leads to greater material degradation.

Influence of the leaching temperature

The effect of the leaching solution temperature on the release of water-soluble products was studied by Fromentin (Fromentin, 2017) for the industrial polyurethane MAPA used in glove box gloves. During these studies, non-irradiated and irradiated polymers were subjected to basic leaching in an inert atmosphere at three temperatures (ambient temperature, 40°C and 60°C). The author observed that the higher the temperature, the greater the TOC and the faster the loss of mass, for both irradiated polymers and non-irradiated polymers. Differences in the leaching kinetics are also observed at ambient temperature compared to the leachings carried out at 40°C and 60°C. This difference appears less significant for irradiated polymers. The differences in the kinetics observed may lead to a problem of representativeness of the data acquired at 60°C to reproduce the behaviour at ambient temperatures.

Influence of the formulation

The type of polymer determines the oxidation rate of the material under irradiation and also its hydrolysis when it is degraded. The higher the polymer's oxidation rate, the higher the release of water-soluble degradation products. This can be explained by a high concentration of oxidised chemical functions such as ketones, esters, carboxylic acids, *etc*.. The more oxidised functions are present in the material, the more they make the material polar and thus allow for the solubilisation of increasingly long carbon chains.

In general, the behaviour of industrial polymers is similar to that of pure polymers, except for their degradation level, which is generally lower than for the pure polymers. The soluble fraction of industrial polymers depends on the polymer's oxidation rate, as for pure polymers. However, the soluble fractions are generally lower, because (i) they contain a percentage by mass of pure polymer ranging from 25% to 95% depending on the material, and (ii) due to the presence of additives, which delays oxidation of the material.

2.5.2 Organic species released by each polymer

Cellulose

The CEA/ORANO performed a characterisation of the water-soluble products released during cellulose (cotton form) degradation under radiolysis/hydrolysis conditions. In these studies, cellulose was irradiated with gamma radiation at 1 MGy and then leached in cementitious water (pH 13.2) at 60°C. The following carboxylic acids were characterized: ISA, acetic, formic, propionic, malonic, adipic and oxalic acids. For ISA, only the isomer α-ISA was dosed. The species identified represent 20% of the total organic compounds present in the leachates. ISA represents 16% of the TOC for non-irradiated cellulose and 3% of the TOC for cellulose irradiated at 1 MGy (Andra).

There is no other data in the literature on species that could be released by hydrolysis of pre-irradiated cellulose. However, studies have been carried out on the hydrolytic degradation of non-irradiated cellulose. The major product generated is ISA, in addition to other acids identified in low quantities, including formic, lactic, glycolic, pyruvic, glyceric, threonic and 2-hydroxybutanoic acids (Glaus *et al*., 1999; Van Loon *et al*., 1999). The kinetics for cellulose degradation by hydrolysis in a cementitious medium and the release of ISA have been studied by two groups: Van Loon and colleagues (Glaus & Van Loon, 1998; Glaus & Van Loon, 2008); Pavasars and colleagues (Pavasars *et al*., 2003).

Polyvinyl chloride (PVC)

The water-soluble degradation products under radiolysis combined with hydrolysis of a soft industrial PVC used as glove-box sleeves have been characterised by the CEA/ORANO. For these studies, the industrial PVC was irradiated under gamma radiation up to10 MGy and then leached in cementitious water (pH 13.2) at 60°C. The species identified/quantified are the following: acetic, formic, glutaric, succinic, adipic, oxalic, malonic, phthalic and benzoic acid (Andra). The release of phthalic acid observed in the case of industrial PVC is associated with leaching of phthalate, present in this substance as a plasticiser (≈ 30% mass). The release of benzoic acid is associated with the degradation of phthalate. The fraction of TOC identified in the leachate is around 49%.

Studies to identify the water-soluble molecules from PVC degradation have also been carried out by RWN (Baston *et al*., 2017). In these studies, the material used was a flexible PVC representative of glove-box gloves, like in the CEA study. In this instance, the polymer contains three different types of phthalates (plasticisers): di-2-ethylhexyl phthalate (DEHP), diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP). The PVC and plasticisers were irradiated at various dose rates (0.25; 0.5; 0.75 and 1 MGy) in the presence of a saturated $Ca(OH)_2$ solution and ambient temperature. Irradiation was also performed at high temperature (80°C) on PVC samples at a dose of 0.75 MGy. The species identified in the RWN studies are: phthalic acid, 2-ethylhexanoic acid, 2-ethyl-1-hexanol and several phenolic compounds (phenol, 2-Isopropylphenol, 3-Isopropylphenol, 4-Isopropylphenol and 4,4-(1-Methyl-ethylidene)-bisphenol).

Ethylene propylene rubber (EPR) copolymer

Two types of EPR copolymer have been studied by the CEA/ORANO, a pure EPR and an industrial EPR in the form of an O-ring. The EPR was chosen as a PE simulant.

The characterisation of water-soluble products from the degradation of these polymers by radiolysis/hydrolysis in cementitious water at 60°C identified and quantified the following species: oxalic, acetic, formic, glutaric, succinic, adipic, malonic and pimelic acid. The contribution of unidentified organic compounds to the TOC increases with the dose; the identified TOC is approximately 4% at 10 MGy (Andra).

2.6 Degradation of ion-exchange resins (IER)

The effects of ionising radiation on ion-exchange resins are similar to those observed for the other organic polymers. The main difference resides in the presence of functional groups grafted onto the polymer skeleton of IERs, which may be subject to cleavage phenomena under radiolysis.

Two cases can be considered for the radiolysis of IERs, differentiating whether radiolysis occurs in the presence of water or under dry conditions. It is also worth mentioning that so-called “dry” resins still contain interstitial water in their structure. Knowledge regarding the behaviour of ion-exchange resins described in the rest of the document refers to resins formed of a polystyrene skeleton.

2.6.1 Radiolytic degradation of "dry" IERs

Degradation of the polystyrene skeleton

The presence of benzene rings in the resin skeleton provides good stability to ionising radiation. Under radiolysis, cross-linkage phenomena are dominant, associated with the production of H_2. Skeleton degradations remain minor up to doses exceeding 10 MGy.

Radiolytic degradation of cationic IERs

For cationic resins, radiolytic cleavage phenomena between functional groups and the organic skeleton are observed for doses exceeding 1 MGy.

Many authors propose mechanisms to explain the radiolytic degradation of cationic resins (Karpukhina *et al.*, 1976 ; Ichikawa & Hagiwara, 1973). For dry resins, the functional groups will be degraded according to a redox mechanism leading to the formation of sulfones by a reaction between two functional groups (note that Ar represents the aryl group in eq. 2-2):

$$\mathrm{ArSO_3H + ArSO_3H \rightarrow ArSO_2Ar + 2H^+ + SO_4^{2-}} \qquad \text{(eq. 2-2)}$$

Radiolytic yields

The gas production radiolytic yields γ ($G_{H2,}$ G_{SO2} and G_{CO2}) have been determined by Gangwer *et al.* for two types of cationic resins, Dowex 50W and KU-2 (Gangwer *et al*., 1977). Gas production radiolytic yield measurements were also carried out by (Traboulsi, 2012) for a cationic resin (Amberlite IR 120) by considering various γ radiation doses under aerobic and anaerobic conditions. The results of (Traboulsi, 2012) indicate that the radiolytic H_2 production is independent of the irradiation atmosphere and the radiolytic yield remains low (lower than 0.10×10^{-7} mol·J^{-1}), similar to that determined by (Gangwer *et al*., 1977) for a Dowex 50W cationic resin.

Radiolytic degradation of anionic IERs

Anionic resins are degraded under irradiation at lower integrated doses than for cationic resins with an identical skeleton. At 0.1 MGy, degradation can already be significant for anionic resins with primary, secondary or tertiary amine functional groups (Pillay, 1986). Many authors also mention a cleavage of functional groups, leading to the formation of nitrogenous compounds, primarily trimethylamine (TMA) (Swyler *et al*., 1983; Rébufa, 2015).

Mechanisms for anionic resin radiolysis and more particularly the degradation of functional groups have been proposed by Ahmed *et al.* (Ahmed *et al*., 1996) and Hall (Hall, 1963). Trimethylamine is formed from a dried resin, by anionic group cleavage following a Hofmann reaction induced under radiolysis (note that Ar represents the aryl group in eq. 2-3):

$$\mathrm{ArCH_3N(CH_3)_3^+,OH^- \rightarrow ArCH_2OH + N(CH_3)_3} \qquad \text{(eq. 2-3)}$$

Radiolytic yields

The gas production γ radiolytic yields of two types of anionic resins in the form containing NO_3^- (Dowex 1 and 11) have been determined by Gangwer *et al.* (Gangwer *et al*., 1977). $G_{H2,}$ for the two resins is about 0.10×10^{-7} mol.J^{-1}. The gas production radiolytic yields of an Amberlite IRA 400 anionic resin were measured by (Traboulsi, 2012) at various doses, under aerobic and anaerobic conditions. The hydrogen gas production radiolytic yield values (from 0.24×10^{-7} mol·J^{-1} to 1.15×10^{-7} mol·J^{-1}) are higher than for cationic IERs. The values of G_{H2} vary with dose in a complex manner. The verified behaviour is not similar to that observed for a large number of polymers, i.e. G_{H2} declines with the dose. According to (Traboulsi, 2013), this complex behaviour may be associated with the degradation of the function groups of the IERs generating amines; these amines may then decompose and also produce H_2. These two degradation stages may occur at different doses and lead to a complex evolution of G_{H2} with the dose.

2.6.2 Radiolytic degradation of IERs in the presence of water

Under the action of ionising radiation, the ion-exchange resins can incur additional degradation caused by the reactive species generated by water radiolysis.

Radiolytic degradation of cationic IERs

The following degradation processes are typically observed for cationic resins irradiated under water:

- cleavage of functional groups at doses exceeding 1 MGy;
- formation of sulfate ions;
- release of volatile products such as H_2, CO_2, CO and methane.

In the presence of oxygen and water, some authors (Kiseleva et al., 1961) note the formation of hydroxylic and carboxyphenolic functions. The form of the resin (H^+ acid or saline form) also influences its stability under radiation. Many authors report that a saturated IER is more radiation resistant (Gangwer *et al*., 1977).

Formation of sulfate ions

In the presence of water, the cleavage of sulfonic groups results in the formation of sulfate ions, in the form of sulfuric acid for resins in H^+ acid form, and a H_2SO_4/counter-ion salt mixture for resins in the saline form. When the resin is initially charged with Fe^{2+} or Fe^{3+} ions, fewer sulfate ions are released (Swyler *et al.*, 1983). Swyler *et al.* (Swyler *et al.*, 1983) showed that the increase in the production of sulfate ions is linear with the dose up to 5 MGy, before levelling out at higher doses.

Radiolytic yields

The radiolytic yield values for gas production were determined by Gangwer *et al.* (Gangwer *et al*., 1977) for a Dowex 50W resin and were also measured recently by the CEA for an Amberlite IR 120 resin. No effect of the irradiation dose (from 0.5 to 4 MGy) on the radiolytic yield values was found for the doses studied (Traboulsi, 2012).

Radiolytic degradation of anionic IERs

The following degradation processes are typically observed for anionic resins irradiated under water:

- loss of the resin's water of hydration and a reduction in grain diameter (Swyler *et al*., 1983; Vannoorenberghe, 1991);
- increase in the pH of the solution in contact with the resin, especially if the resin is charged with OH^- species;
- cleavage of functional groups at doses exceeding 0.1 MGy;
- production of nitrogenous compounds (primarily TMA);
- release of H_2 gas and traces of methane and CO_2.

As for cationic resins, radiolysis leads to the loss of the quaternary ammonium functional group, and in some cases, the formation of hydroxylic and carboxyphenolic groups, which are slightly acidic cationic exchange sites in the anionic resin network.

Radiolytic yields

Baidak and Laverne (Baidak & Laverne, 2010) have studied the influence of the water content of an Amberlite 400 anionic resin with quaternary ammonium in three different forms (Cl^-, NO_3^-, OH^-) on the radiolytic yield for H_2 production. The results show that for resins in Cl^- or OH^- form, H_2 production increases with higher water content, whereas the resin in NO_3^- form has lower H_2 production for equivalent water contents.

The CEA performed γ irradiation to determine the radiolytic yields of H_2 production for the same type of anionic IER in the OH^- form (Amberlite 400). Irradiation was performed under water in anaerobic conditions at doses between 0.5 and 4 MGy. The radiolytic yield seems to increase slightly up to a dose of 3 MGy (from 0.68×10^{-7} mol·J^{-1} to 0.99×10^{-7} mol·J^{-1}) (Traboulsi, 2012).

Radiolytic degradation of mixed-bed resins

The radiolytic yields of H_2 production under γ radiation have been measured by the CEA. The resins studied consisted of a mixture of 25% mass of anionic resin (in OH^- form) and 75% mass of cationic resin (in H^+ form). The radiolytic yield values are relatively low and appear to increase for doses exceeding 3 MGy (from 0.04×10^{-7} mol·J^{-1} to 0.46×10^{-7} mol·J^{-1}).

2.6.3 Leaching of ion-exchange resins

Post-irradiation leaching of ion-exchange resins is studied in order to assess the behaviour of these materials with regard to the coupled phenomena of radiolysis and hydrolysis. The information provided in this section was acquired through studies carried out by the CEA for cationic, anionic and mixed-bed resins (Traboulsi, 2012).

Leaching of post-irradiation anionic resin at 4 MGy

The quantity of Total Organic Carbon (TOC) in a leaching solution for an anionic resin that has previously been irradiated under "dry" and anaerobic conditions at 4 MGy was followed during 140 days. The release of water-soluble compounds occurs very quickly after the irradiated resin is placed into contact with pure water. The cumulative quantity of TOC released by the resins changes little as a function of leaching time, from 8 mg·g^{-1} to 18 mg·g^{-1} of dry resins.

The following main species were identified during the leaching of pre-irradiated resins: acetic acid, formic acid, TriMethylAmine (TMA), DiMethylAmine (DMA), MonoMethylAmine (MMA) and the NH_4^+ ion.

Leaching of post-irradiation cationic resin at 4 MGy

The quantities of TOC released from non-irradiated resins are higher for the cationic resin than for the anionic resin studied. According to (Traboulsi, 2012), the release of TOC from the cationic resin is most probably due to the presence of admixtures used in the industrial resin manufacturing process. As for the anionic resin, cationic resins irradiated in the presence of water release little TOC. However, the presence of air during irradiation increases the quantity of TOC released by the leaching of this material. This release of water-soluble species increases above a dose of 4 MGy (to around 25 mg·g^{-1} of dry resins).

Post-irradiation leaching of a mixed-bed resin MB 400

For a pre-irradiated mixed-bed resin, the quantities of TOC released after 1 day of leaching are low for most irradiation conditions. Under oxidising conditions, the release of TOC only becomes significant for radiation doses exceeding 4 MGy (around 25 $mg \cdot g^{-1}$ of dry resins).

Comparison of the TOC quantities released by the mixed-bed resin compared to those released by the fully cationic or anionic resins shows that:

- for doses up to 1 MGy, the quantities of TOC released by the mixed-bed resin remain below those released by its cationic and anionic components considered separately, regardless of the irradiation conditions (anaerobic or aerobic medium, presence of water, *etc*.);
- for irradiation in an anaerobic or aerobic medium with a dose of approximately 4 MGy, the quantities of TOC released by the mixed-bed resin are close to those of its cationic component.

The following main water-soluble species are released during post-irradiation leaching of mixed-bed resins: acetic acid, formic acid, oxalic acid, TMA, DMA, MMA, ammonium ion and SO_4^{2-}.

2.6.4 Degradation of IERs under the effect of temperature

IERs are especially sensitive to the influence of temperature. Under the action of temperature, three consecutive degradation reactions occur:

- loss of absorbed humidity and the water of hydration contained in the resin (80 - 120°C);
- cleavage of functional groups grafted onto the resin's polystyrene skeleton (50-150°C);
- decomposition of the resin's polystyrene skeleton (> 150°C).

For cationic resins, the sulfonic functional group is stable. The bond cleavage reaction between the sulfonic functional group and polymer skeleton occurs at between 120-150°C (Li & Sengupta, 2000). For anionic resins, the Hofmann degradation can transform quaternary ammonium functional groups (strong bases) into tertiary amines (weak bases), or even fully degrade the functional group. This reaction occurs in an alkaline media. The Hofmann degradation only significantly occurs above 50°C. Degradation of the polystyrene skeleton occurs at a high temperature and its carbonisation only observed at around 300°C.

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3. Organic-cement interactions

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This chapter summarizes the current understanding of the behaviour of organic molecules in cement-based materials.

Organic materials can be present in ILW and LLW radioactive waste. As seen in the framework of the CORI Task 2 and the previous SOTA chapter, the origin of these organic compounds is varied and includes (i) radiolysis and/or hydrolytic degradation of cellulosic materials, polymers, ionic-exchange resins (IERs) or other organic materials, (ii) wastes from effluent extraction processes such as EDTA, NTA, TBP, and (iii) cementitious admixtures such as superplasticisers. These compounds are subject to degradation processes that can release organic molecules to solution. The products that are formed are, to some extent, controlled by the specific chemical conditions imposed by the cement-based materials in the repository. Some of these degradation products are ligands which can react with radionuclides to form complexes in solution (Allard, 2005; Allard and Ekberg, 2006; Androniuk, 2017; Androniuk *et al.*, 2017; Boggs *et al.*, 2010; Colàs, 2014; Colàs *et al*., 2013; Dario *et al.*, 2004; Evans, 2003; Felipe-Sotelo *et al*., 2012; Gaona *et al*., 2008; Garcia *et al.*, 2020; González-Siso *et al*., 2018; Holgersson *et al*., 1998; Holgersson *et al*., 2011; Keith-Roach, 2008; Pointeau *et al*., 2006; Tasi *et al*., 2018a, 2018b; Thakur *et al*., 2006; Tits *et al*., 2002; Vercammen, 2000; Vercammen *et al*., 2001). The complexation of the radionuclides by organic ligands can cause an increase in their mobility by (i) increasing their solubility and (ii) decreasing their sorption to cement-based materials (Ochs *et al*., 2014).

In order to understand the mechanisms enhancing the mobility of radionuclides as organic complexes, this chapter describes the fundamental properties driving the behaviour of organic molecules in the presence of cement-based materials. This overview of organic molecules includes (i) their properties in solutions related to cementitious environments, (ii) their sorption behaviour, and (iii) their diffusion behaviour.

3.1 Properties in solution

The properties of organic molecules in solution are characterized by their speciation and their solubility (Hummel *et al*., 2005). According to IUPAC conventions, the analytical composition of a saturated solution, expressed in terms of the proportion of a designated solute (*e.g.* M^i or Org^i) in a designated solvent, is the solubility of that solute. The solubility may be expressed in a number of ways, including as a concentration, molality, mole fraction, or mole ratio. Solubility considers not just the amount of free ion, M_i, in solution but the sum of all aqueous species of the M^i as shown in eq.3-1, where L^k stands for the different ligands (hydroxyl ion, organics, *etc*.) present in solution.

$$Solubility = [M]_{TOTAL} = [M^i] + [ML^{i+k}] + \left[ML_2{}^{i+2k}\right] + \ldots \quad \text{(eq. 3-1)}$$

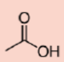
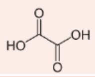
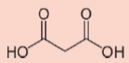
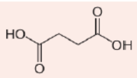
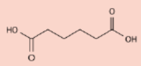
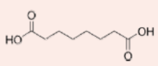
The distribution of all aqueous chemical species of M^i or Org^i in a system is defined as the element chemical speciation by IUPAC and is therefore dependent on the nature of the solution. For example, the speciation of calcium in basic solution is predominantly Ca^{2+} and $CaOH^+$. However, in the presence of organic molecules such as gluconate, the complex species Ca(OH)(HGlu)(aq) and $Ca(HGlu)^+$ can appear (Gaona *et al*., 2008), and can be the predominant forms at high gluconate concentrations.

The speciation of an element or an organic compound under a given set of conditions can be estimated through thermodynamic calculations based on data integrated into a thermodynamic database. This database includes the necessary parameters for each species related to their properties in solution. As an example of this, *TABLE* 3-1 and *TABLE* 3-2 detail the source and chemical structure, respectively, of the organic molecules deemed important from a radioactive waste disposal perspective that are considered in ThermoChimie (Giffaut *et al*., 2014), a thermodynamic database managed by the French (Andra), British (RWM) and Belgian (Ondraf-Niras) waste management agencies. Organic ligands are commonly considered as its negatively charged form as indicated in *TABLE* 3-1; note that *TABLE* 3-2 includes the general structure of the main organic ligands but does not reflect their most common protonation state. *TABLE* 3-3 provides a matrix of the element complexation data available for these organic molecules in ThermoChimie.

TABLE 3-1*: List of the main organic ligands and their sources considered in ThermoChimie database (www.thermochimie-tdb.com).*

Organics in wastes	Organic ligands in ThermoChimie
Cement additives*	Gluconate
Plastics, Filters, Resins**	Adipate
	Phthalate
Bitumen degradation products	Oxalate
	Acetate
Cleaning/extraction agents	EDTA
	NTA
	Citrate
Cellulose degradation products	Isosaccharinate
Organic species in clay***	Malonate
	Succinate
	Suberate

TABLE 3-2*: Structure of organic ligands currently considered in the ThermoChimie database.*

Monocarboxylic	Acetic	
Dicarboxylic	Oxalic	
	Malonic	
	Succinic	
	Adipic	
	Suberic	

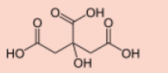
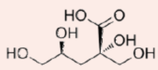
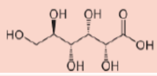
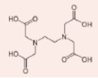
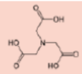
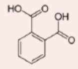
Hydroxycarboxylic	Citric	
	ISA	
	Gluconic	
Aminocarboxylic	EDTA	
	NTA	
Aromatic Carboxylic	Phthalic	

***TABLE 3-3**: Availability of key thermodynamic data for various organic/species complexes; the considered species are radionuclides and/or major ions such as Ca and Mg. (ThermoChimie, version 10a, 2016).*

	Monocarboxylic	Dicarboxylic					Hydroxocarboxylic			Aminocarboxylic		Aromatic carboxylic
	Acetic	**Oxalic**	**Malonic**	**Succinic**	**Adipic**	**Suberic**	**Citric**	**Gluconate**	**ISA**	**EDTA**	**Nta**	**Phthalic**
acid/base	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Ca	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓
Mg		✓	✓	✓			✓			✓	✓	
Ni	✓	✓	✓				✓		✓	✓	✓	✓
Eu	✓	✓	✓	✓					✓			✓
Am	✓	✓					✓	✓	✓	✓	✓	✓
Cm		✓										✓
Tc	✓	✓								✓	✓	
Th	✓	✓	✓	✓			✓	✓	✓	✓	✓	
U	✓	✓		✓			✓	✓	✓	✓	✓	✓
Np	✓	✓					✓	✓	✓	✓	✓	
Pu	✓	✓						✓	✓	✓	✓	✓

✓ Data available in ThermoChimie vs. 10a

The work on the solubility of Ca(α-ISA)$_2$(s) and (CaGLU)$_2$(s) by Van Loon *et al.* (1999) is a good illustration of how thermodynamic data can be used to predict the concentrations of organic species in solution. From the reported thermodynamic constants, Van Loon *et al.* were able to estimate the maximum concentration of α-ISA and gluconate that might be expected in a cement pore water (Van Loon *et al*., 1999). Importantly, this estimation took into account stage I and II degradation of the cement-based materials (see Chapter 5 of this SOTA), and thus provided realistic concentrations to be expected under repository conditions, as illustrated in *TABLE* 3-4.

***TABLE 3-4**: Calculated maximum concentrations of α-ISA and gluconate in the cement pore water for different stages of cement degradation (Van Loon et al., 1999).*

Stage	pH	[Ca]/ mM	I^a/ M	$[\alpha\text{-ISA}]_{max}{}^b$/ mM	$[\text{GLUC}]_{max}{}^b$/ mM
I	13.3	2	0.3	44	930
II	12.5	20	0.05	10	220

^{a}*I*, ionic strength. ^{b}Calculated by eqn. (12).

3.2 Sorption on cement-based materials

In the context of underground waste repositories, cement-based materials will contribute not only as structural materials but will also influence the behaviour of species (radionuclides, organics, *etc*.) in solution in terms of retention and stabilization (Berckmans *et al*., 2013). The retention properties of the cementitious materials can be very strong for some radionuclides such as actinides or lanthanides (Albrecht *et al*., 2005; Ochs *et al*., 2010, Wang *et al*., 2008; Wieland 2014), as further discussed in Chapter 4 of this SOTA.

Relatively little information is available on the sorption of organic molecules to cement-based materials, although this is a relevant effect to consider within an integrated description of sorption phenomena. The existing information suggests that low-weight organic molecules (propionic acid, formic acid for instance) are weakly sorbed in cement-based materials (Wieland *et al*., 2016, see *FIGURE 3.6*). On the other hand, some organic ligands (*i.e.* ISA, gluconate, EDTA, NTA, ...) can be strongly sorbed, and in the specific case of citric and oxalic acids, even precipitation can occur (Dario *et al*., 2004) under the presence of Ca cations. The high amount and volume of cement-based materials in a repository, even if sorption of a certain organic molecule may be rather low per unit mass, suggests that they may significantly impact the behaviour of organic molecules.

The interactions of isosaccharinic acid (ISA) with cement-based materials have been investigated by several authors, and are now described as a good example in more detail. As the main degradation product of cellulose, ISA has been particularly studied because of (i) the high quantity of cellulose in the waste streams and (ii) its complexing properties for radionuclides (see references). The sorption of ISA on cement pastes and on C-S-H/C-A-S-H phases, the main hydration products of cement pastes (see SOTA Chapter 5 on fundamental cement chemistry), has been studied by Van Loon & Glaus (1998). *FIGURE* 3-1 and *FIGURE* 3-2 present the amounts of sorbed ISA for two ISA diastereomers, α-ISA and β-ISA. Note that α-ISA has been extensively studied because of (i) the very well know synthesis process, and (ii) higher expected sorption and complexation capacities than β-ISA (Brinkmann *et al*., 2019).

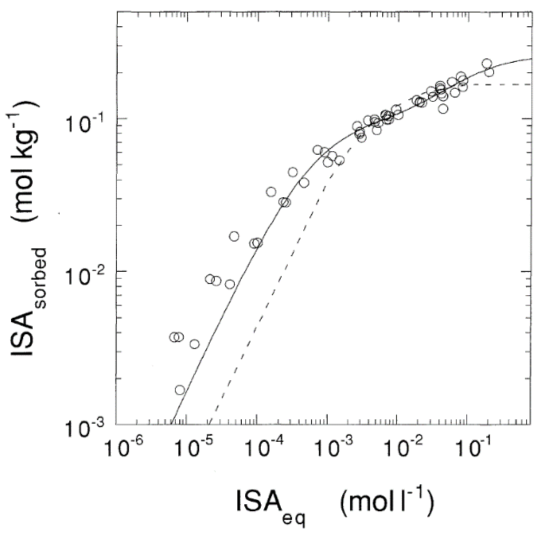


***FIGURE 3-1**: Sorption isotherm of on Portland cement at pH=13.3. Empty circles stand for experimental data, the solid line represents the modelling considering a two-sites-Langmuir model and the dashed line a one-site Langmuir model. (Van Loon & Glaus, 1998).*

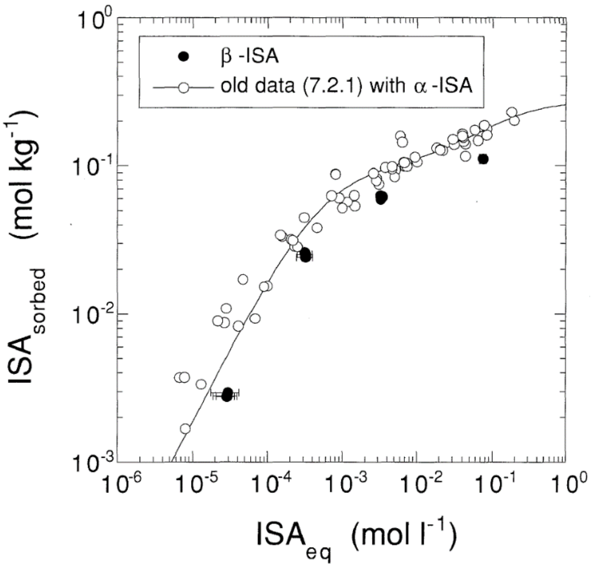


***FIGURE* 3-2**: *Sorption isotherm of β-ISA on Portland cement at pH=13.3. Solid line indicates the modelling of the data obtained for α-ISA using a two-sites-Langmuir model (Van Loon & Glaus, 1998).*

FIGURE 3-3 shows the sorption isotherms for α-ISA on C-S-H and C-A-S-H phases. These results confirm that C-S-H/C-A-S-H phases can make a significant contribution to the sorption of ISA on cement-based materials.

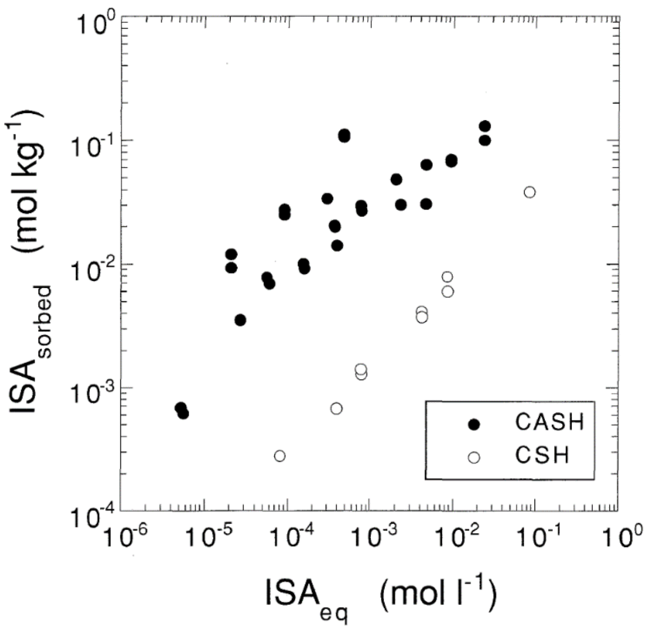


***FIGURE* 3-3**: *Sorption isotherm of α-ISA on C-S-H and C-A-S-H phases at pH=13.3 (Van Loon & Glaus, 1998).*

FIGURE 3-4 displays sorption data for ISA and gluconate on hardened cement pastes for degradation stages I (pH=13.2) and III (pH=11.9) as function of time (Pointeau *et al*., 2006). These results show a kinetic evolution of the sorption for both ISA and GLU: as expected, the sorbed content increased during the first days (3 days for stage I and 10 days for stage III) but a decrease was then observed until a near-complete desorption was observed. As proposed by the authors, this desorption process could be explained by a carbonation of the HCP grains as (i) cement-based materials are very sensitive to carbonation and (ii) sorption tests of ISA and GLU on calcite ($CaCO_3$) under pH 13.3 conditions showed no sorption. Calcite could be formed at the surface of the HCP grains and, consequently, that would prevent the sorption of ISA and GLU. This assumption is important because host-rock waters contain carbonate ions which could promote the degradation of cement pastes to stage IV also called carbonated state (see SOTA Chapter 5).

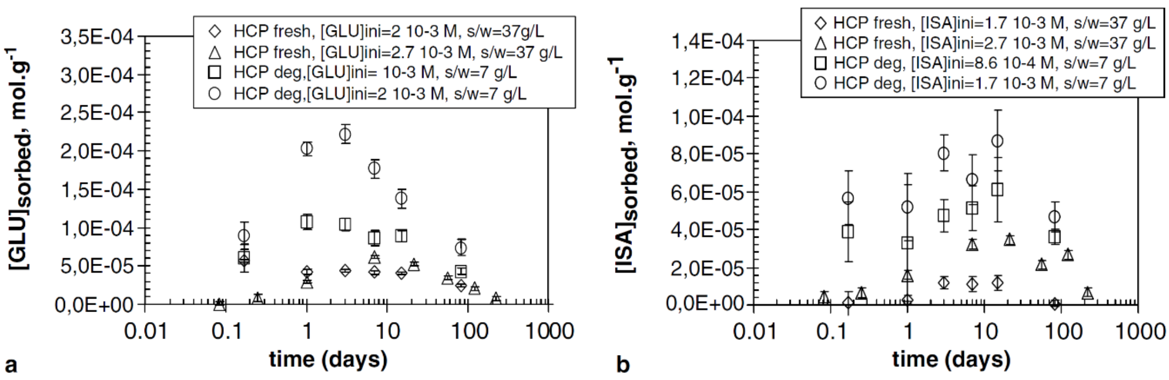


***FIGURE* 3-4**: *Evolution of (a) gluconate (GLU) and (b) ISA contents (mol·g^{-1}) sorbed on fresh (stage I) and degraded (stage III) cement pastes (Pointeau et al., 2006).*

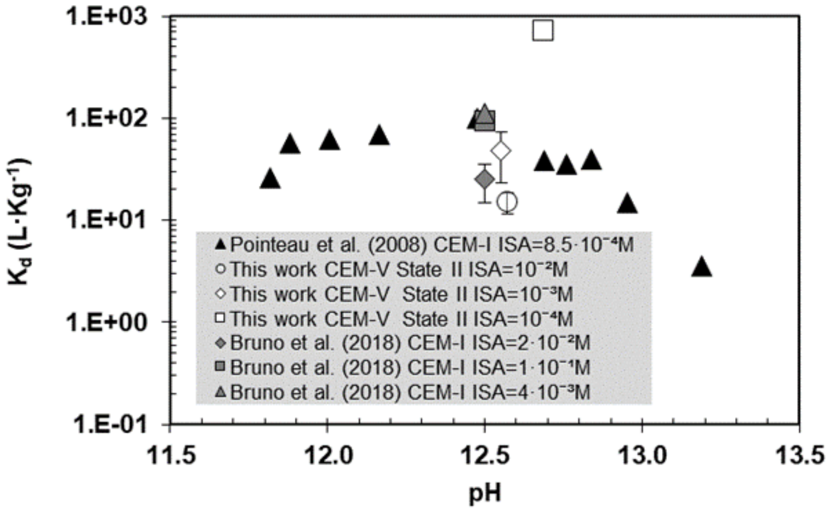


***FIGURE* 3-5**: *Comparison of adsorption distribution coefficients (K_d) for ISA against pH in fresh and degraded cement pastes. Non-filled symbols are results from Garcia et al. (2020) (´this work´ in the legend); black filled symbols by Pointeau et al. (2008); grey filled symbols by Bruno et al. (2018).*

More recently, Bruno *et al*. (2018), Garcia *et al.* (2020) and Pointeau *et al.* (2008) studied the sorption of ISA on cement pastes at degradation stage II. Pointeau *et al.* (2008) and Bruno *et al*. (2018) studied CEM I cement pastes whereas García *et al*. (2020) studied CEM-V (see SOTA Chapter 5 for a description of the different cement degradation stages). A comparison of the results from these studies is provided above in *FIGURE* 3-5*.* The results show that the sorption affinity of ISA for the two cement types is similar, except for the lowest ISA concentration studied.

Despite being less studied in the literature, the adsorption of small organic molecules on cement pastes is known to be very low. Wieland *et al*. (2016) obtained distribution coefficients for several low molecular weight organic compounds such as acetic and formic acid, formaldehyde, acetaldehyde, methanol, and ethanol. *FIGURE* 3-6 shows the evolution of the uptake of these organic molecules as a function of reaction time; the distribution coefficients obtained (≤1 L·kg^{-}1) are much lower than those obtained for ISA (K_d ≈ 100 L·kg^{-1}).

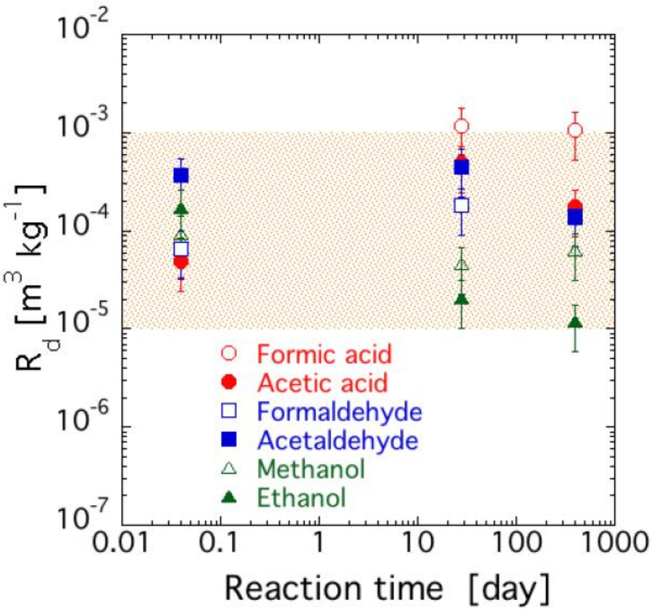


FIGURE 3-6*: Uptake of low molecular weight organic compounds by HCP as a function of reaction time.*

3.3 Diffusion in cement-based materials

The relevant theoretical concepts and the main equations are given in more detail in sub-chapter 4.4 of the present SOTA.

Very few studies (Chida and Sugiyama, 2008; Kaneko *et al*., 2003; Matsumoto *et al*., 1995; Sasoh, 2008; Wieland *et al*., 2016) are available on the diffusion of organic compounds through cement pastes, mainly because of the poor mobility of organic compounds in compacted materials such as cement pastes. Overall, the available studies focused on small organic compounds (acetic acid, acetaldehyde, ethanol, formaldehyde, formic acid and methanol) providing only rather limited information on the diffusion and sorption properties of the cement pastes. Wieland and co-workers concluded in their work that acetate (CH_3COO^-) diffusion could be fairly well explained with one-site model, while formate ($CHOO^-$) diffusion required an additional parameter indicative of a second sorption site (Wieland *et al*., 2016). This means that even a relatively small difference in the organic carbon chain, from 1 carbon to 2 carbons, may have a significant impact on the organic sorption behaviour due to the limited available pore space in the diffusion experiments.

3.4 Conclusion

For cementitious materials, little information is available on the behaviour of organic compounds, especially so in comparison with clay-rock materials. That can be explained by challenges arising from the large range of systems (in terms of degradation states and cement formulations), and by the properties of organic species in solution at high pH (in terms of speciation). Even if a general behaviour of the organic molecules in cementitious systems cannot be foreseen at this time, some works on argillaceous materials proposed correlations between the molecular properties (molecular mass, dipolar moment, partition factor) and the transfer properties of organic molecules (solid/liquid distribution coefficient, K_d and effective diffusion coefficient, D_e) which could be extended to cement-based materials (Dagnelie *et al*. 2014, 2018); Rasamimanana *et a*l. 2017).

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4. Radionuclide-organic-cement interactions

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This chapter provides an overview of the current knowledge on radionuclide and organic ligands interactions under cementitious environments, focusing on the specific species selected in WP3 CORI.

4.1 Introduction to WP CORI Task 4 objectives

In any international radioactive waste disposal concept, including surface disposal, near surface or deep geological disposal (Andra, 2005; Ochs *et al.,* 2016), the main objective of a multi-barrier system is to prevent radionuclides (RN) from spreading into the environment. After the breach of the primary waste containers, the aim is to slow down as much as possible the dispersion of the radionuclides progressively released from these containers. To guarantee the long-term safety of radioactive waste disposals, one of the main research challenges is to provide a robust understanding of all the processes controlling RN interactions within the materials composing the system. The multi-barrier system is made up of the waste packages, the man-made engineered barriers and, for deep geological disposal, the host rock (geological barrier).

Cementitious materials are amongst the main constituents of waste packages and the engineered barriers for low and intermediate level radioactive waste (L/ILW) disposal. They are typically used as encapsulation matrix, package material, backfill and structural material because their mechanical resistance. These materials, mainly grouts, mortar or concrete, are porous; meaning that they are composed of a solid matrix with reactive surfaces and a porewater with a chemical composition specific for cementitious materials (see SOTA Chapter 5), characterised by highly alkaline pH conditions.

The main processes controlling RN migration are: solubility, retention processes and physical transport.

- The chemical speciation of RN and eventually precipitated solubility limiting solid phases in cementitious pore water govern their solubility. Depending on the chemical composition of the pore water (pH, redox potential E_h, major matrix ions, ligands …), RN can form different chemical species with potentially distinct chemical behaviour.
- The retention or uptake of RN in cementitious environments is the result of interactions between the dissolved radionuclide species in solution and the surface of the cementitious solid matrix material. This important parameter can be quantified by determining (*e.g.* in batch experiments) the solid/liquid distribution coefficient, $K_{d,,}$ [$L \cdot kg^{-1}$] which represents the ratio between the RN concentration adsorbed onto the solid and the RN concentration remaining in the porewater at equilibrium. Adsorption is one of the most important retention processes, but other processes as (co)precipitation, formation of new minerals or solid solutions may trap RN in the solid matrix irreversibly.
- Radionuclide transport processes in porous materials are induced by several possible gradients (chemical, electric, hydraulic...). That leads to different physical phenomena encountered in the disposal concepts, such as advection and / or diffusion. A key process being studied in cementitious materials is the diffusive transport induced by chemical gradients, like the concentration gradient. Diffusion is quantified by diffusion coefficients which are both species- and material-specific.

Knowing the source term of radionuclides in the waste packages, the combination of the three above-mentioned processes allows explaining the reactive transport (migration) of the RN through the cementitious barrier. All factors affecting RN chemical speciation / solubility and their interactions with mineral surfaces are relevant for contaminant migration. Thus, a thorough analysis of all the factors and mechanisms that can contribute to contaminant mobility is required. This fundamental knowledge is necessary to predict RN behaviour and assess the long-term safety of a repository, minimise the associated risks and support management decisions.

When some additional chemical species are released in a disposal system in significant amounts, *i.e.* organic molecules in the present case, they can affect RN behaviour. The presence of organics is a main cause of contaminant mobility enhancement (Means and Crear, 1978; Santschi *et al.*, 2017). The impact of organic molecules on RN migration is related to RN-organic complexes formation, that increase RN solubility and/or inhibit RN retention on solids (Hummel *et al.*, 2005a and reference therein). Even if these particular effects have been known since a long time, they are far from being elucidated and described in a scientifically advanced mechanistic way (Keith-Roach, 2008). Therefore, it is still very difficult to predict them adequately. EURAD-CORI aims to improve this situation.

The presence of anthropogenic organics is a particular case in L/ILW disposal, mainly because their amount is higher than the organics naturally present in a geological formation and additionally feature a high degree of chemical diversity. As reported in previous in Chapter 2 and 3 of this SOTA, many different types of plastic wastes (halogenated polymers as polyvinyl chloride PVC, non-halogenated polymers as polythene PE), papers, woods, rubber or ion exchange resins (IER) are co-stored with the contaminants. Over time, they can lead to a large variety of degradation products in addition to the organic complexants (EDTA, NTA, …) disposed of as part of certain waste products.

The impact of organic molecules on RN migration depends on many factors: (i) the type and concentration of organics, (ii) the surrounding solid and aqueous phases which will provide the physicochemical scenario (pH, E_h, ionic strength, type of ion in solution), and (iii) on the characteristics of the contaminant itself (sorption capability, speciation, hydrolysis…). The organic degradation products present in radioactive disposal and the inventories change from one country to another (Abrahamsen *et al.*, 2015). This means that the overall performance can be considered as *site-specific*. To make reliable predictions of RN migration under a wide range of conditions, detailed understanding at the fundamental level is required. CORI Task 4 works to improve the knowledge on organic-radionuclide complexes mobility in cement-based systems by providing mechanistic understanding of interaction processes and provide detailed and new quantitative experimental data.

The cementitious materials and organics studied in CORI Task 4 are prioritised in view of their applied and scientific relevance and are consistent with CORI Tasks 2 and 3:

- CEM I and CEM V cements are used as raw materials for cementitious samples preparation, considering different degradation stages. Amongst the main mineral phases considered, C-S-H (calcium silicate hydrates, $(CaO)_x(SiO)_y(H_2O)_n$) and C-A-S-H (calcium alumina silicate hydrates, $(CaO)_x(SiO)_y(Al_2O_3)_z(H_2O)_n$) will be studied considering different CaO/SiO_2 molar (C/S) ratios;
- organic ligands include, ISA (isosaccharinic acid, $C_6H_{12}O_6$), EDTA (ethylenediaminetetraacetic acid, $C_{10}H_{16}N_2O_8$), adipic acid ($C_6H_{10}O_4$), phthalic acid ($C_8H_6O_4$) or short-chained carboxylic acids, as well as the degradation products that are identified in CORI Task 2. Finally, organic cement additives as superplasticizers are also considered.

The main radionuclides studied in CORI Task 4 are: nickel isotopes; uranium isotopes; actinides (III/IV) mainly Am, Cm, Pu and Th and/ or chemical homologues as, for example, Eu.

4.2 Radionuclide chemistry in cementitious environments

4.2.1 Speciation/solubility under alkaline conditions

The first information needed to assess the behaviour of radionuclides in cementitious materials, regards their chemical speciation under alkaline conditions. In a cementitious pore water, the speciation is specifically controlled by the interactions with the ubiquitous hydroxyl "OH^-" ions that create hydrolytic species but also other major/minor dissolved ions or neutral species (see Guillaumont *et al.*, 2003 and especially the recent update from Grenthe *et al.*, 2020 for the main actinides U, Np, Pu, Am and Tc).

The properties of both radionuclides and organic molecules in solution are characterised by their speciation and their solubility (Hummel *et al.*, 2005a). According to IUPAC conventions, the analytical composition of a saturated solution, expressed in terms of the proportion of a designated solute (*e.g.* M^i or Org^i) in a designated solvent, is the solubility of that solute. The solubility may be expressed in several ways, *e.g.* concentration, molality, mole fraction, or mole ratio. Solubility does not consider just the amount of the free ion, (M^i) in solution but the sum of all aqueous species of M^i as shown in eq. 4-1, where L^k stands for the different ligands (hydroxyl ion, organics, *etc*.) present in solution.

The thermodynamic solubility is one of the most important parameters to consider in migration studies as it represents the capacity of a given solid phase to dissolve under given geochemical boundary conditions and defines the maximum possible concentration in the aqueous phase of the elements composing it.

$$Solubility = [M]_{TOTAL} = [M^i] + [ML^{i+k}] + \left[ML_2{}^{i+2k}\right] + \ldots \qquad \text{(eq. 4-1)}$$

The distribution of all aqueous chemical species of M^i or Org^i in a system is defined by IUPAC as the element chemical speciation and is therefore dependent on the nature of the solution.

In general, the precipitation of a contaminant to form a solid (non-colloidal) phase is often favourable from an environmental point of view, because it limits the contaminant concentration in the aqueous phase and limits its transport. Precipitation (or co-precipitation) can be a relevant retention/uptake process under the alkaline conditions generated by cementitious materials. However, the complexation phenomena existing between radionuclides and certain organic molecules (ligands) influence the RN speciation by eventually outcompeting hydrolysis under alkaline to hyperalkaline pH conditions. RN-organics complex formation is potentially related to significant changes in RN solubility.

4.2.2 Speciation/solubility in the presence of organic ligands

Regarding speciation/solubility of RN in the presence of organic ligands, the OECD Nuclear Energy Agency review work remains a major reference (Hummel *et al.*, 2005b; carried out within the framework of the Thermochemical Database Project NEA-TDB Phase II). The work focused on the complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr, as well as interactions with the major competing elements Na, K, Mg and Ca with selected organic ligands (oxalate, citrate, EDTA and α-ISA). This is a very extensive work but still not complete. Rather few information for the conditions of interest is available for trivalent actinides, Np, Pu(IV), U(IV) and for Th(IV) since a quite large variability in the experimental data has been detected and, above all, because data are rarely obtained under the hyperalkaline conditions typical for cementitious environments (Felipe-Sotelo *et al.*, 2015). NEA-TDB is preparing an update of the previous organics volume within the current Phase V.

Two additional reviews carried out by Gaona *et al.* (2008) and Rai and Kitamura (2017) enrich the selection on available thermodynamic data concerning complexation of RN by ISA and/or gluconic acid (GLU), present as gluconate species in alkaline to hyperalkaline pH conditions. In the work of Gaona *et* *al.* (2008), the available thermodynamic data for An(IV)–ISA/GLU complexes have been reviewed and re-calculated to ensure the internal consistency of the stability constants assessed. Further modelling exercises, estimations based on Linear Free-Energy Relationships (LFER) among tetravalent actinides, as well as direct analogies between ISA and GLU complexes have also been performed. This approach has led to the definition of a speciation scheme for the complexes of Th(IV), U(IV), Np(IV) and Pu(IV) with ISA and GLU forming in alkaline to hyperalkaline pH conditions, both in the absence and presence of calcium. Rai and Kitamura (2017) reviewed and recommended equilibrium constant values for ISA complexation reactions involving Ca, Fe(III), Th, Np(IV), and U(VI). The authors considered that the available data for Pu(IV), U(IV), and Am(III) were extremely limited and based on ill-defined/controlled experimental techniques and should be used for scoping studies only. Obviously, even for the most studied organic ligands like ISA, many knowledge gaps on contaminant-organic interaction reactions still exist. Another similar example from the literature are the reported stability constants for actinide-EDTA complexes that vary by orders of magnitude (Cartwright *et al.*, 2007).

A more recent experimental study in the ISA system was performed by Tasi *et al.* (2018) providing the most comprehensive thermodynamic dataset available to date for the system Pu^{3+}–Pu^{4+}–OH^-–Cl^-–ISA^-–$H_2O(l)$, that is valid under a wide range of conditions relevant for nuclear waste disposal (see *FIGURE 4-1* below).

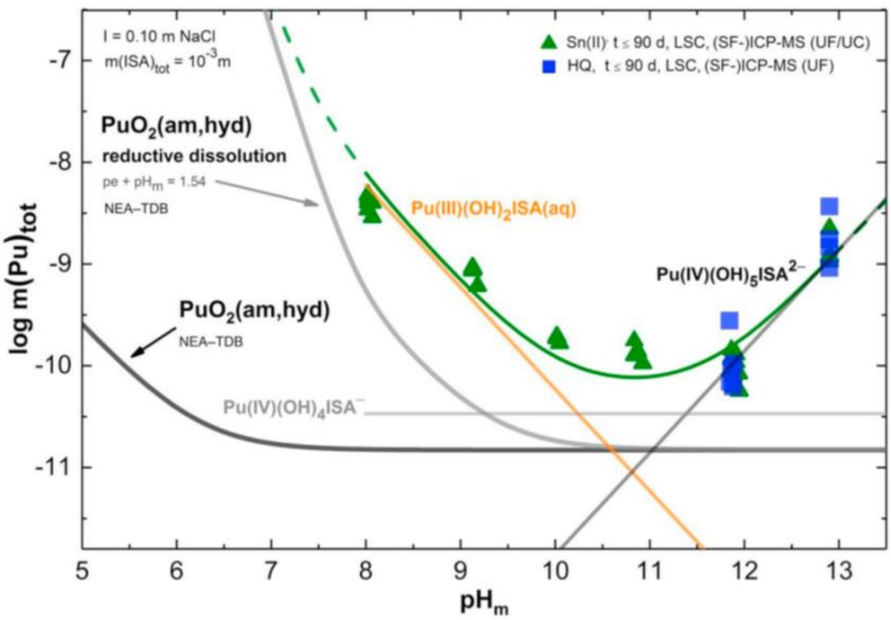

FIGURE 4-1*: Experimentally measured $m(Pu)_{tot}$ in equilibrium with PuO_2(ncr,hyd) at I = 0.10 m NaCl in Sn(II)-buffered systems with pH_m=8.0–12.9 in the presence of $m(ISA)_{tot}=10^{-3}$ m and in hydroquinone-buffered systems, at pH_m > 11 with $m(ISA)_{tot}=10^{-3}$ m.*
Solubility curves (solid and dashed) in green (with m $(ISA)_{tot}=10^{-3}$ m) for Pu(IV)O_2(ncr,hyd) in the presence of ISA are calculated (at I = 0.10 m NaCl) using the chemical and thermodynamic models derived by Tasi et al. (2018). Black and grey solid lines correspond to the thermodynamically calculated solubility of PuO_2(am,hyd) in the absence of ISA, calculated using equilibrium constants reported in the NEA-TDB (Guillaumont et al., 2003) (Fig. 4-1 taken from Tasi et al., 2018).

It should be noted that the Supporting Information linked to this paper by Tasi *et al.* provides a recent “Review of previous experimental studies on the complexation behaviour of ISA with tri- and tetravalent actinides” by the same authors.

Considering other organic ligands targeted in CORI, *i.e.* for instance adipate, a study from Fromentin and Reiller (2018) needs to be mentioned. The authors investigated the complexation of Eu(III) by adipic acid, a major hydrosoluble degradation product of γ-irradiated polyesterurethane. The formation of a complex between Eu^{3+} and $Adip^{2-}$ was confirmed by time resolved laser-induced fluorescence spectroscopy (TRLFS) investigations and the complexation constant was extrapolated from experimental data. This led to a discussion of previous data published by Wang *et al.* (2000). Using the same kind of spectroscopic properties, Wang *et al.* (1999) had also studied the complexation of lanthanide(III) with aliphatic dicarboxylic acids, and particularly with phthalate, isophthalate and terephthalate. Fromentin and Reiller (2018) concluded that the formation of $EuAdip^+$ could only occur at weakly acidic to mildly basic pH values (4 < pH < 9). Under the studied conditions (0.3 mol kg_w^{-1} adipate / 0.5 mol kg_w^{-1} $NaClO_4$) adipate does not seem to be able to complex Eu(III) and outcompete hydrolysis in alkaline media with pH >10. A predominance diagram of the Eu(III)-adipate system is given below in *FIGURE* 4-2.

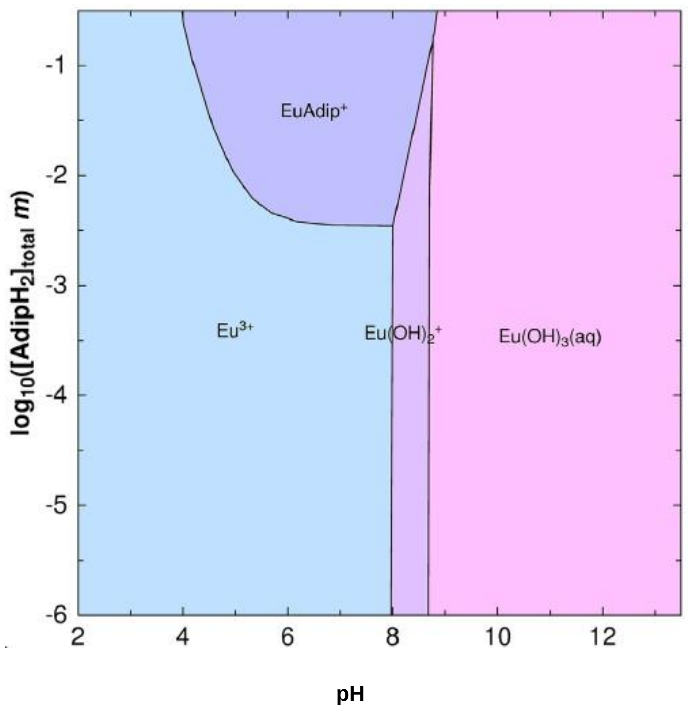

FIGURE 4-2*: Predominance diagrams of Eu(III) 10^{-6} mol·kg_w^{-1} vs. pH with increasing total adipic acid concentration, I=0.1 mol·kg_w^{-1} ($NaClO_4$) at $P(CO_2)=10^{-12}$ atm. Diagram obtained using Phreeplot software (Kinniburgh and Cooper, 2011) (Fig. 4-2 taken from Fromentin and Reiller, 2018).*

Very recently in 2020, Fromentin *et al.* (2020) studied interactions between hydro-soluble degradation products from a radio-oxidized polyesterurethane and Eu(III). In their work (using gamma irradiation at 1000 kGy and 31 days in a pH 13.3 artificial cement water at 60°C), the main hydro-soluble degradation products are adipic acid and butane-1,4-diol. The use of TRLFS showed the existence of several types of Eu(III) complexes depending on pH ranges. The fluorescence of europium was investigated as a function of total organic carbon content and pH and has indicated at least two relevant Eu(III) complexes. However, it should be noticed that the interpretation of complexation at pH > 10, and especially at pH 13.3, is not straightforward.

The workability of cements is usually improved by the addition of organic additives like superplasticizers, a group of several different chemical substances. Several studies have been dedicated to the complexation of RN or heavy metals by such molecules under cementitious environments (Glaus *et al*., 2003; Young, 2012; Wieland *et al*., 2014; García *et al.*, 2018a; Baston *et al.*, 2019).

4.2.3 Speciation/solubility calculations

Predictive geochemical modelling is commonly used to assess the chemical speciation of an element in a specific environment. Predictions are developed based on thermodynamic equilibrium modelling and speciation software, *e.g.* PHREEQC geochemical code (Parkhurst and Appelo, 2013). Apart from the NEA-TDB Project mentioned earlier, which provides a most valuable set of critically reviewed and consistent thermodynamic data recommended for use but is as such not complete in terms of the systems and species covered, other specific thermodynamic databases were developed in the field of radioactive waste management with clearly better usability.

The PSI/Nagra Chemical Thermodynamic Database 12/07 (PSI/Nagra TDB 12/07; Thoenen *et al.*, 2014) was prepared to support the ongoing safety assessments in the framework of the “Sachplan Geologische Tiefenlager” for the planned repositories for low- and intermediate-level and for high-level radioactive waste in Switzerland.

The ThermoChimie database (Giffaut *et al.*, 2014) is managed by the French, Belgian and British waste management agencies; Andra, Ondraf-Niras and RWM, respectively. Since its initial creation by Andra in 1996, ThermoChimie has been based on *(i)* previous thermodynamic database compilations; *(ii)* open scientific literature; *(iii)* data obtained by means of specific experimental programs on actinides and fission products carried out under the auspices of Andra or other reputable experimental programs endorsed by Nuclear Waste Management organizations and research institutions; *(iv)* estimations (Giffaut *et al.*, 2014). Thus, as shown in *TABLE* 3-3, a large number of RN thermodynamic data addressing the systems studied in CORI are available in this database.

Organic ligands can have a significant impact on RN complexation reactions in the aqueous phase and hence on radionuclide speciation and/or solubility. Based on thermodynamic databases, these effects can be constrained by (geo)chemical calculations in several cases, although a significant numbers of ligand systems remain under-defined. In the preparation phase of EURAD CORI it was decided that CORI shall not carry out studies specifically targeting the development of new thermodynamic data for databases. Several data gaps remain open for these indispensable fundamental input data. Data which are required in order to establish a detailed scientific mechanistic understanding of radionuclide-organic-cement ternary systems.

4.3 Radionuclide uptake in cementitious materials

4.3.1 Uptake onto cementitious materials

Exhaustive studies have been carried out during the past decades to derive quantitative data and mechanistic understanding of radionuclide uptake onto cementitious materials. These works were mainly performed in the context of radioactive waste disposal and take into account (i) different kinds of cementitious materials, (ii) the influence of their different potential degradation stages on chemical processes, and (iii) the uptake onto several constitutive pure phases (see SOTA Chapter 5).

The uptake is quantified by a solid liquid distribution coefficient noted K_d (or distribution ratio R_d) (generally in $L \cdot kg^{-1}$) and defined by:

$$K_d = \frac{C_{ads}}{C_e} = \frac{n_0 - n_e}{m} \frac{V}{n_e} \qquad \text{(eq. 4-2)}$$

where C_{ads} ($mol \cdot kg^{-1}$) is the concentration of adsorbed species per mass of sorbent, C_e ($mol \cdot L^{-1}$) the concentration of the species in solution at equilibrium, n_0 (moles) and n_e (moles) the initial and equilibrium molar quantity in solution, V is the volume of solution and m is the dry mass of solid sorbent.

The distribution coefficient is an experimentally determined parameter quantifying the distribution of a chemical species between a given fluid and solid material sample under certain conditions, including the attainment of constant aqueous concentrations of the species of interest. This parameter represents the sum of all the phenomena that are able to remove an element from the aqueous phase, *i.e.* by adsorption on the surface of the solid matrix, incorporation inside some of the solid matrix mineral phases or precipitation in solution with other species. The most relevant retention process often is adsorption. To isolate the contribution of adsorption processes on radionuclide retention, precipitation must be avoided in experiments with respect to the respective solubility limits.

In the particular context, the scientific community benefits from two important reviews published in 2016 and 2018.

The first one is the book “Radionuclide and Metal Sorption on Cement and Concrete” from Ochs *et al.* (2016) published by Springer. This book contains a full state-of-the-art assessment and a critical evaluation of the type and magnitude of sorption and incorporation processes in hydrated cement systems, responsible for the retention properties of cementitious materials towards radionuclides and metals from a variety of radioactive and industrial waste. In Ochs *et al*. (2016), the sorption values for Cl, I, Cs, Sr, Ra, Ag, Ca, Ni, C, Th, U, Pu, Np, Pa, Am, Se, Mo, Tc, Pd, Pb, Nb, Sn, H, Be, Zr are summarized and the original studies referenced. This review was commissioned by Ondraf-Niras in the context of near-surface disposal and contributes to improved process understanding and scientific argumentation. It is used for selecting “best estimate” sorption values for the radionuclides/metals and deriving lower and upper limits for these values.

The second publication (Tits and Wieland, 2018) is based on the research programme that had been carried out for many years by the Laboratory for Waste Management (LES) at the Paul Scherrer Institute in Switzerland with the aim to understand the interaction processes of actinides and lanthanides with cementitious materials both on a microscopic and macroscopic scale. This PSI public report contains an overview of batch sorption studies with actinides and lanthanides in different redox states and on various cementitious materials carried out at the LES. The actinides and lanthanides investigated include Eu(III) and Am(III), Th(IV), Np(IV), Np(V) and Np(VI) and U(VI). The experimental results and interpretations provided in this report aim to:

- quantify the actinide/lanthanide uptake by hardened cement paste (HCP) and C-S-H phases,
- describe the effects of cement paste / C-S-H composition, cement pore water composition and pH on actinide/lanthanide sorption by cementitious materials, and
- discuss the mechanisms driving the uptake of actinides by cement paste and C-S-H phases.

The aim of the present SOTA is not to copy and repeat previously published work .The entire book by Ochs *et al.* (2016) was dedicated to such a detailed bibliographic review. We strongly encourage readers to refer to both previously mentioned documents, which provide a relatively exhaustive bibliographic base on a specific cementitious material/radionuclide system. In combination with the work performed in CORI Task 3 on binary systems (cement/organic), the work planned in CORI Task 4 on ternary systems (cement/organic/radionuclide) extends knowledge beyond the present State-of-the-Art.

4.3.2 Uptake in the presence of organic ligands

Many of the studies about the effects of organics on RN retention/uptake can be considered as only quasi-qualitative, as their aim is to compare retention values of the contaminant in the presence or absence of the organic component. This basic approach, merely based on direct experimental evidences and no comprehensive system understanding, may not be enough for safety assessment of nuclear waste disposals (Payne *et al.*, 2013) in certain cases. The numerical value of the distribution coefficient depends on several factor (pH, ionic strength (I), adsorbate concentration, *etc*..) K_d values cannot be extrapolated to conditions different from those adopted in the experiment and therefore a strong motivation exists to establish a full mechanistic approach based on detailed scientific understanding.

In their recent review about the possible *“reduction of radionuclide uptake in hydrated cement systems by organic complexing agents”*, carried out for the Swedish Nuclear Fuel and Waste Management Company (SKB), Ochs *et al.* (2014) examined the fate of different RN or other species (C, Ca, halogens, Cs, alkaline earth elements, Ag, Cd, Pd, Ni/Co, An(III)/Ln(III), Ac, An(IV), An(V), An(VI), Zr, Sn, Tc, Nb, Se, Mo, Pb, Po) in the presence of ISA, EDTA, NTA, GLU, citrate, oxalate and degradation products of a UP2 filter aid. The study was as far as possible based on experimental evidence directly applicable to the ternary systems considered. The finding was that much of the information was only available for ISA, and the conclusions for many other ligands were based on ISA by analogy. This can be understood as a lack in well-established experimental data.

Cellulose degradation under hyperalkaline conditions, conditions typical of cementitious environments, leading to the isosaccharinic acid, ISA (Pavasars *et al.*, 2003), is a quite well-established process. ISA is probably the most studied organic ligand in the frame of radioactive waste disposals because it has shown high capacity to complex radionuclides (Humphreys *et al.* 2010; Kuippers *et al.*, 2018 and references therein), especially actinides.

Diesen *et al.* (2017) studied the impact of cellulose degradation products, present as a mixture in an artificial cement pore water (pH 12.5). Different amounts of Eu(III), as freshly precipitated solid europium hydroxide, were added to this mixture. After filtration, Portland cement was added to the solutions. From their measurements, the authors concluded that under the experimental conditions applied, the extent of adsorption of the formed organic europium complexes to cement was low (<9 µmol $Eu \cdot g^{-1}$ of cement) in comparison to data for adsorption of europium onto cement without the presence of organic degradation products reported in literature. Their study stressed the need for further information regarding the mobility of these complexes under disposal conditions.

The possible effects of competitive ions (Na, Ca or Fe) on ISA-RN complexation have been mentioned in the literature, but the information necessary for a better description of their overall role is not enough (Kuippers *et al.*, 2018).

Organic products with chelating functions (EDTA or nitrilotriacetic acid, NTA) may be present in appreciable concentration in many nuclear installations. They are mainly generated during effluent extraction processes. Many different studies showed its capability of strongly chelating tri- and tetravalent actinides (May *et al.*, 2012; Reinoso Maset *et al.*, 2012) enhancing their mobility in different substrates. EDTA was clearly involved in RN migration at the Oak Ridge National Laboratory, USA, (Killey *et al.*, 1984). However, Reinoso-Maset *et al.* (2013) also showed that this effect is not the same for all the organic-RN systems. For example, the mobility of Cs within silica/sand was not affected by the presence of EDTA. EDTA has also a limited effect onto U migration, probably due to the presence of other cations in solution (Mg, Ca) which may form stronger complexes with EDTA than U. The presence of other ligands (as, for example carbonates, phosphates) are particularly important in U retention, and thus the competition between organic ligand (and inorganic) should be considered as well.

A mechanistic approach to the understanding and description of retention processes in complex materials like cement needs the application of a bottom-up approach, focusing on the behaviour of the main sorbing minerals (*e.g.* C-S-H phases). Molecular dynamic simulation is an appealing modern technique to increase the knowledge on mechanisms of RN-organic and cement interactions. In particular, Androniuk and Kalinichev (2020) and Androniuk *et al.* (2017) analysed U and GLU interactions with C-S-H.

Concerning retention data, the studies on the potential role of cement superplasticizers on RN suggest that their impact on RN mobilisation should be negligible (Wieland *et al*, 2014; NDA, 2017; Garcia *et al*., 2018b; Baston *et al*., 2019). However, not much is known about the long-term evolution of cement-bound superplasticizers in hardened concrete. Some authors mention that uncertainties remain as to whether RN behaviour would be the same when studying crushed or intact material. There is a lack of fundamental understanding on that subject.

In some cases, the presence of organics has been observed to increase contaminant adsorption (Kornilovich *et al.*, 2006; Barger and Koretsky, 2011), hypothetically due to the formation of solid-organic-contaminant (S-O-C) ternary complexes, adsorbed on the solid surfaces.

A mechanistic analysis of RN-cement-organic interactions needs focused experiments to understand the extent of the effects of organics on RN retention, but also a thermodynamic description of the aqueous and solid species formed.

4.4 Radionuclide diffusion in cementitious materials

Diffusion is one of the most important transport processes in porous media. Diffusion is controlled by concentration gradients. Therefore, ions and molecules generally move from regions with high concentration to regions with lower concentration. The determination of diffusion coefficients in cement is important not only for describing RN migration, but also for predicting the movement of all the ions that can contribute to cement degradation affecting its main properties.

It is out of the scope of the present document to deal in detail with the mathematic treatment of diffusion, which is widely addressed in the literature (*e.g.* Crank, 1975). We would simply remind that the diffusion theory is based on the first and second Fick's laws. The first Fick's law states that the mass flux per unit cross-sectional area, F [$kg\cdot m^{-2}\cdot s^{-1}$], is directly proportional to the concentration, C [$kg\cdot m^{-3}$], gradient and, for a one-dimension simplification, is expressed as:

$$F = -D\frac{\partial C}{\partial x} \qquad \text{(eq. 4-3)}$$

The diffusion coefficient, D [$m^2\cdot s^{-1}$] is the proportionality constant between concentration gradient and flux and determines the rate at which ions and/or molecules spread. The concentration of ions/molecules in the porewater, C, depends on time t [s] and distance x [m] , and the conservation of the mass leads to the Fick's second law, expressed in its one-dimensional approximation as:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad \text{(eq. 4-4)}$$

It is important to remark that diffusion in porous media is more complex than in free water, as it is affected by the characteristics of the solid material, especially its porous structure. The variable geometry of solid structures is defined by geometric terms such as tortuosity (τ) or constrictivity (δ), which cannot be straightforwardly measured. Not all the pores are connected and the volume available for diffusion and contributing to solute transport is related to connected pores. Thus, in porous media, the cross-sectional area available for diffusion is limited by its porosity (ε).

The diffusion coefficient of a species in free water, D_w, will be related to the diffusion coefficient in a porous material, D_p, in the following way:

$$D_p = \frac{\delta}{\tau^2} D_w \qquad \text{(eq. 4-5)}$$

The effective diffusion coefficient, D_e, takes account of the smaller cross-sectional area available for diffusion in porous media and is defined by:

$$D_e = \varepsilon \cdot D_p \qquad \text{(eq. 4-6)}$$

Another mechanism that affects diffusion in the cementitious porous media is the retention on the solid surfaces, because it retards ions migration. To account for retention processes, it is necessary to define another parameter, the apparent diffusion coefficient, D_a, which is defined as:

$$D_a = \frac{D_e}{(\varepsilon + \rho \cdot K_d)} = \frac{D_e}{\alpha} \qquad \text{(eq. 4-7)}$$

ρ is the dry density of the solid and α is a parameter known as capacity factor, which includes retention through the distribution coefficient, K_d. If a solute is non-sorbing ($K_d = 0\ m^3 \cdot kg^{-1}$) then the capacity factor is equivalent to the porosity.

To determine these transport parameters different experimental set-ups must be designed, based on the characteristic of the RN or ion that shall be studied. Depending on the constraint of the experiment, different analytical solutions to the Ficks' laws exists (Crank, 1975) but experimental results can also be analysed by numerical methodologies. The most used classical experimental techniques to measure the diffusion coefficients of chemical species are: Through-Diffusion (TD); In-Diffusion (ID) and Out-Diffusion (OD) (Flury and Gimmi; 2002).

Even if diffusion processes in HCP, concrete, or mortars have been studied over the last years, data available in the open literature are relatively scarce. Most of data deal with diffusion of conservative tracers as tritiated water (HTO) or Cl^- , I^- or low sorbing species (Atkinson and Nickerson, 1984; Sarrot *et al.*, 1991; Bucur *et al.*, 2010; Felipe-Sotelo *et al.* 2014; van Es *et al.*, 2015; Akagi *et al.*, 2018; Shafikhani and Chidiac, 2019).

Some compilation of diffusion coefficients from safety analyses studies exist (Albinsson *et al.*, 1993; Mattigod *et al.*, 2001; Wieland, 2014) which are often related to the specific materials and/or chemical conditions of interest for each repository design. In general, markedly different diffusion behavior are observed for different cement formulations (Grambow *et al.*, 2020).

Due to the specific property of each cementitious material, it is difficult to draw strong general conclusions. Nevertheless, for the same formulations, it can be stated that D_e decreases when the water to cement ratio decreases (being the material less porous) (Jakob *et al.*, 1999; Yamaguchi *et al.*, 2009).

The scarceness of diffusion data in cement-based materials can be partly explained by the experimental difficulties related to the work with them. The chemical conditions generated by the cement, implies high adsorption and/or low solubility for many elements, thus diffusion tests with moderately and high sorbing species need long time (in the order of months to years). This means that in through diffusion experiments, even after several months, the RN may not have appeared in the outlet deposit. Similarly, in in-diffusion experiment, the diffusion profile may be too short (just several micrometers) to be adequately analyzed. In these cases, only the upper limit of diffusion coefficients can be estimated, but not the real one. The application of new methodologies for diffusion experiments as microprobe techniques are certainly welcomed to partially overcome these drawbacks. For example, Suyiama *et al.* (2008) analyzed uranium diffusion in OPC and another Portland cement containing 30% ash (FAC) analyzing the diffusion profiles by laser ablation microprobe inductively coupled plasma mass spectrometry and determining both D_e and D_a (for OPC: $D_a = \sim 4 \times 10^{-16}\ m^2 \cdot s^{-1}$; $D_e = \sim 3 \times 10^{-11}\ m^2 \cdot s^{-1}$, and for FAC: $D_a = \sim 2 \times 10^{-17}\ m^2 \cdot s^{-1}$; $D_e = \sim 6 \times 10^{-13}\ m^2 \cdot s^{-1}$).

Furthermore, it is quite complicated to maintain the physicochemical conditions and the cementitious materials stable during the whole experiment duration. Dissolution/precipitation processes may take place, resulting in changes within the solid (*e.g.* porosity, mineralogy). RN incorporation within existing or freshly formed phases may occur, and the existence of no-reversible retention processes can also entangle the interpretation of diffusion data. This means that, often, simple diffusion/retention models cannot be applied for the interpretation of diffusion data. The lack of data is reflected also in the studies about RN diffusion in the presence of organic ligands, that are much less available compared to retention *batch* experiments.

For what concerns the effects of the organic on RN diffusion, some information can be found on cellulose degradation products. Holgersson *et al.* (1998) analyzed the effects of gluco-isosaccharinate on the diffusion process of Cs, Ni, Pm and Th in a Portland cement by means of through diffusion experiments.

The authors observed only the breakthrough of HTO and Cs, but not of Ni, Pm or Th. The effect of the organic on Cs diffusion was considered negligible.

Felipe-Sotelo *et al.* (2016) analyzed the migration of selenium in cementitious backfill (Nirex reference vault backfill, NRVB, and PFA/OPC) in the presence of cellulose degradation products. No sign of breakthrough was evidenced after one year, for either of both solids, in agreement with the very low solubility of selenium under alkaline conditions and presence of Ca. Felipe-Sotelo *et al.* (2017) also analyzed U and Th diffusion through intact cylinders of NRVB by in-diffusion experiments and did not observe breakthrough for either U or Th, both in the absence and presence of cellulose degradation products.

Detailed quantitative data about RN-organic complexes diffusive transport in cementitious materials remain a largely open issue.

4.5 References Chapter 4

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5. Fundamental cement chemistry

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This chapter summarizes fundamental aspects and knowledge on the chemistry of cement-based materials.

Cement-based materials have been massively used in civil engineering for more than one hundred years. They also represent a main component in radioactive waste disposal facilities, in terms of being considered for use as engineered barriers and packages. The chemistry of ordinary cement is well-known. In particular, H.W.F. Taylor (1992) in his outstanding work described the main cement components and their hydration processes. The minerals formed by the hydration of cement, called cement hydrates, have been deeply characterized during the last decades. The Calcium Silicate Hydrates (C-S-H) are the main cement hydrate; they are closely related to the fundamental properties of cement-based materials. This is explaining the large number of scientific papers on this cement hydrate.

This document presents a synthesis of the cement chemistry according to the current cement types, outlining the anhydrous cement composition and the different hydrated phases. Finally, the chemical evolution of the cementitious matrix in the context of a deep geological repository is described.

5.1 Anhydrous cement

The chemical properties of the cement-based materials and their mineralogy depend on the chemical composition of cement (Taylor, 1992). Different types of cement are available; their use depends on the environmental exposure (sulfate for instance), the design of the concrete structure (massive elements for instance), or the economical point of view (use of Supplementary Cementitious Materials). Consequently, this section presents the main components of the ordinary cement and the various types of cement made with Supplementary Cement Materials (SCMs).

The solid phases in anhydrous cement are expressed in the form of oxides such as CaO, SiO_2, Al_2O_3 and Fe_2O_3, which are the main components. The nomenclature of these oxides is defined as follows:

- C = CaO
- A = Al_2O_3
- S = SiO_2
- s = SO_3
- F = Fe_2O_3
- M = MgO
- c = CO_2

Cement powder is a mix of clinker and gypsum (around 5%). The main components of clinker are: (i) C3S (alite), (ii) C2S (belite), (iii) C3A, and (iv) C4AF (Taylor, 1992). This composition corresponds to the ordinary Portland cement called CEM I. Other types of cement are mixes composed of cement CEM I and SCMs. The main SCMs are (i) blast-furnace slag, (ii) fly ash, and (iii) silica fume (Lothenbach *et al*., 2011; Snellings *et a*l., 2012). Binary, ternary and even quaternary cements can be made with these supplementary materials. We can distinguish the cement types (i) CEM III composed with CEM I and slag, and (ii) CEM V, a ternary cement composed by CEM I, fly ash and slag. The ternary diagram in *FIGURE* 5-1 illustrates different types of cement and their components regarding their Ca, Si and Al contents.

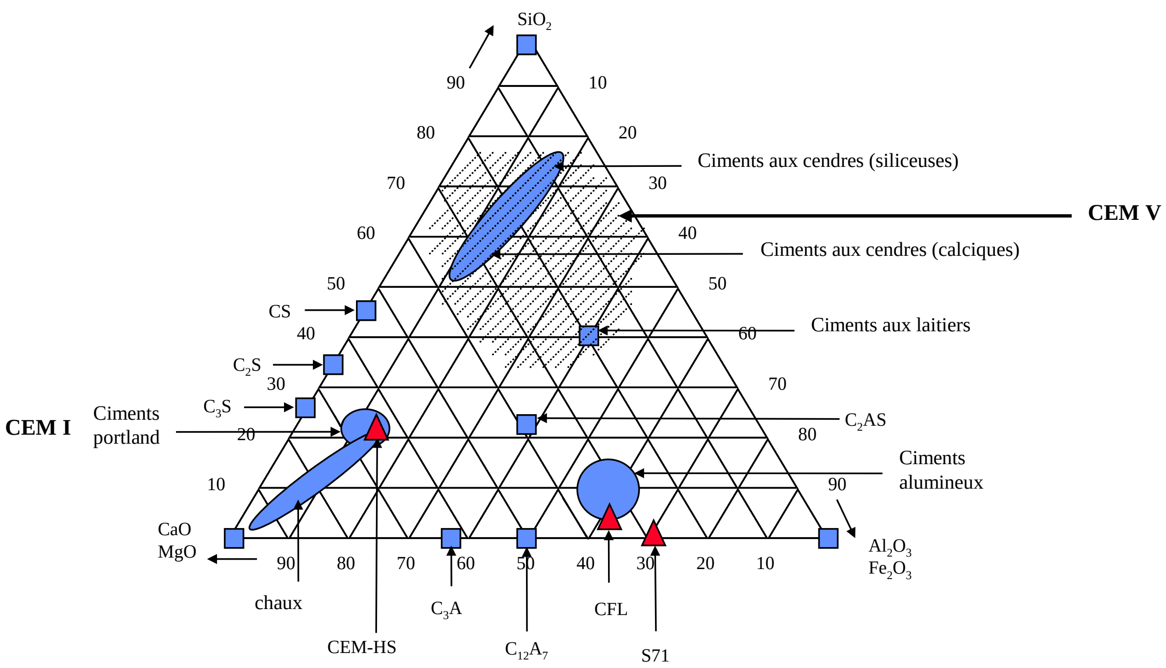

***FIGURE 5-1**: Ternary diagram CaO-SiO$_2$-Al$_2$O$_3$ showing the compositions of the main types of cement (from Damtoft et al., 1999).*

5.2 Cement hydrates

Once cement is hydrated with water, solid phases including water molecules are formed. These mineral phases are called cement hydrates. Hydration of C3S and C2S leads to the formation of Calcium Silicate Hydrates (C-S-H) and portlandite (CH), while ettringite (AFt), AFm phases, and calcium alumina hydrates are formed from C3A and C4AF (Taylor, 1992; Strutzman, 1999; Glasser, 2011). Because of their high specific surface area, C-S-H mostly contribute to the radionuclide retention capacity. However, the other minerals can also contribute, especially AFm phases, for some radionuclides.

Regarding their significant impact of the radionuclide behaviour and on the overall properties of cement-based materials, C-S-H are specifically described in terms of thermodynamic (Gartner & Jenings, 1987; Chen *et al*., 2004; Lothenbach & Nonat, 2015; Walker *et al.,* 2016) and, also, electrokinetic properties (Nachbaur *et al*., 1998; Viallis-Terrisse *et al*., 2001; Henocq, 2005). One of the main characteristics of C-S-H is the variable stoichiometry characterized by the molar ratio Ca/Si (C/S) between 0.6 and 1.7. This stoichiometry can be illustrated by the relationship between the C/S and the calcium concentration in solution as illustrated in *FIGURE* 5-2.

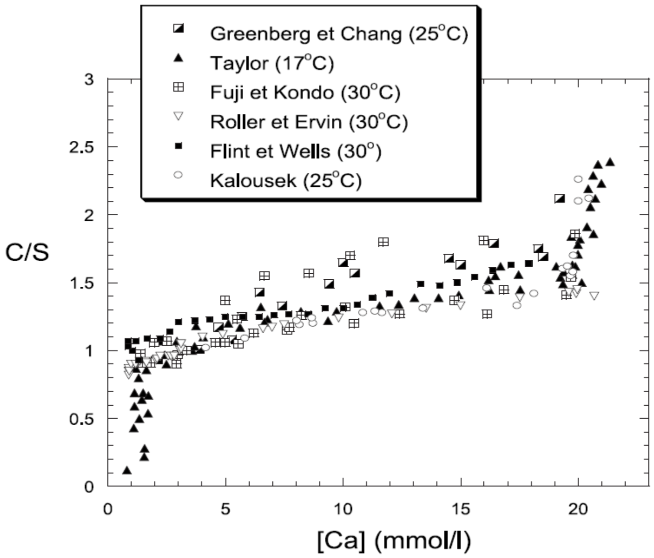

***FIGURE 5-2**: Solubility of C-S-H: C/S as a function of calcium concentration in a solution in equilibrium with the C-S-H from Berner (1992) and Henocq (2005).*

In a pristine cement-based material, the C/S ratio of C-S-H is expected to be higher than 1.45 (near 1.75 (Taylor, 1993); 1.7 (Jennings, 2000)). That means, according to *FIGURE* 5-2, that the degradation of cementitious materials is associated with a decalcification of C-S-H. Nevertheless, it is important to note that in sound cement-based materials, the initial alkali content in the pore solution induces a high pH (pH>13) and modifies the chemical equilibrium of C-S-H by decreasing the calcium concentration in solution as shown in *FIGURE* 5-3 (Hong & Glasser, 1999; Henocq, 2005).

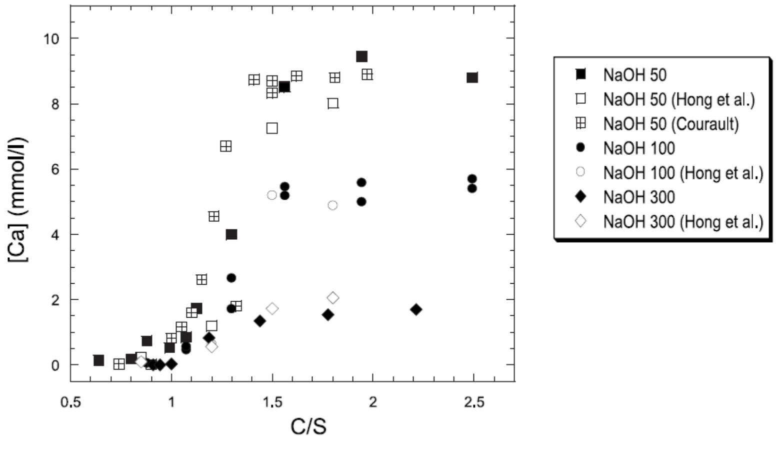

***FIGURE 5-3**: Solubility of C-S-H: calcium concentration as a function of C/S for different NaOH concentrations (from Henocq, 2005).*

The characterization of the main cement hydrates in terms of thermodynamic properties such as solubility have motivated many works of interest (Damidot *et al*., 2011; Lothenbach & Winnefeld, 2006; Roosz *et al*., 2018), not only on C-S-H as aforementioned, but also on AFm phases (Matschei *et al*., 2007), ettringite (Myneni *et al*., 1998; Perkins & Palmer, 1999), and portlandite (Duchesne & Reardon, 1995).

C-S-H have a nanostructure defined by the *dreierketten* chain structure (Hamid, 1981). The nanostructure evolves as a function of C/S ratio. As shown by ^{29}Si NMR technique in *FIGURE* 5-4, this evolution is characterized by long silicon tetrahedra chains for low C/S ratio (Q_2 tetrahedra) which are gradually broken as the C/S ratio increases (Q_1 tetrahedra) (Cong & Kirkpatrick, 1996; Zanni *et al*., 1996; Klur *et al*., 1998; Roosz *et al*., 2018). In parallel, there is also an evolution of the amount of layers per C-S-H grain: for C-S-H (C/S=1.0), stacks of 3 of 6 layers were observed while for C-S-H (C/S=1.2), particle stacks of 4 to 8 layers were observed (Gaboreau *et al*., 2020). These structure evolutions with C/S ratio involve a decrease of the specific surface area as C/S increases. Consequently, that has consequences on the sorption properties.

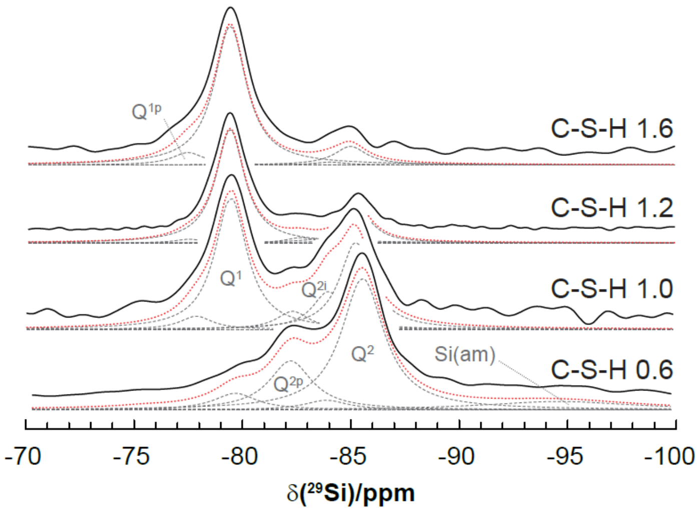

FIGURE 5-4*: ^{29}Si NMR spectra of C-S-H samples with various C/S ratios (from Roosz, 2016).*

For ordinary cement, C-S-H is the main hydration product together with CH. However, for cement-based materials that include SCMs, the alumina content is much higher than ordinary cement, and as a consequence, alumina substitution into the C-S-H structure occurs to form C-A-S-H (Faucon *et al*., 1998; L'Hôpital *et al*., 2015). The physico-chemical properties of C-A-S-H are assumed to be similar to those of C-S-H in terms of alkali sorption (Bach *et al*., 2013; Chappex & Scrivener, 2012) contrary to the observations by Hong & Glasser (2002). Regardless of these chemical aspects, the hydration of cementitious mixes with SCMs involved a pozzolanic reaction between portlandite produced from C3S and C2S, and silica and alumina released from the hydration of SCMs (*FIGURE* 5-5). The effect of the pozzolanic reaction is a densification of the matrix with more C-(A)-S-H, decreasing the transport and improving mechanical properties.

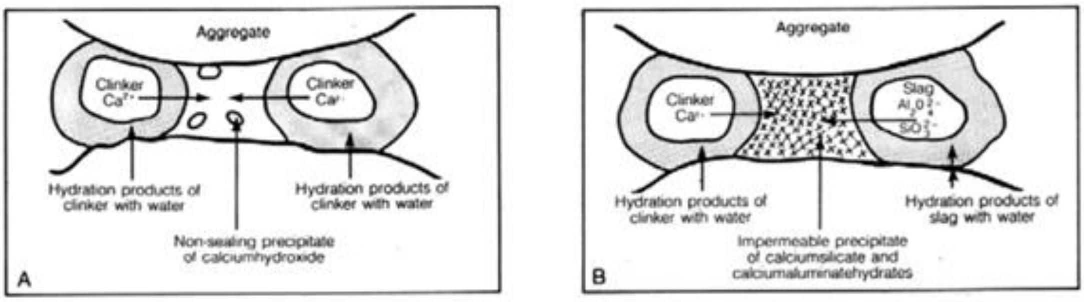

***FIGURE 5-5**: Effect of the pozzolanic reaction: A) hydration of ordinary Portland cement, and B) hydration of a cement/slag mix (from Surech & Nagaraju (2015)).*

As aforementioned, the other main cement hydrates are ettringite, AFm phases, hydrotalcite and possibly hydrogarnet or gypsum. These solid phases, even if their content and specific surface area can be negligible compared to the ones of C-S-H, have a role in terms of radionuclide retention (oxy-anions for ettringite and AFm) and chemical evolution in certain environments (sulfate attack for example).

5.3 Pore solution

The cement-based materials are porous materials with a porosity around 10% for concrete and 40% for hydrated cement pastes (HCPs) (Fagerlund, 2006; Tracz, 2016). For pristine materials in fully saturated conditions, this porous volume is filled with a solution in equilibrium with the cement hydrates. For ordinary cements, the pore solution composition is controlled by the portlandite solubility and the alkali content implying a high pH and, consequently, alkaline conditions. Andersson *et al*. (1989) characterized the pore solution of hydrated cement pastes for various cement types including the major ionic species as well as E_h and pH. This work showed that the composition of the pore solution is dependent on the chemical composition of cement but generally controlled by NaOH and KOH contents which imply a high pH (~13.3). Moreover, Andersson *et al*. (1989) mostly measured a positive redox potential E_h (~100 mV), i.e. oxidizing conditions, expect when blast-furnace slag was used in the material and reducing conditions were observed (E_h = -377 mV).

The chemical composition of cement may include toxic chemicals or other species as trace elements which then can be present in the pore solution at trace concentrations. The main trace elements are mostly Ba, Ni, Sr, Pb, Co or Li (Hillier *et al*., 1999; Achternbosch *et al*., 2005; Young, 2012). The trace elements can be released in the environment under leaching and, probably, could compete with radionuclides in terms of sorption. Additionally, they can also participate in ion-exchange with active elements as described in González-Siso (2018).

As an example, *TABLE* 5-1 gives the concentration of the main species in the pore solution of a CEM V hydrated cement paste (Olmeda *et al*., 2017).

***TABLE 5-1**: Pore solution composition from CEM-V/A HCP samples at 102 days of curing (Olmeda et al., 2017).*

Pore solution properties	
pH	13.3
Species	Concentration (mmol/kg)
Ca	1.4
S	1.6
Na	72
K	210

5.4 Superplasticizers

Cement admixtures are an essential component of concrete. Usually, they are used for enhancing the workability of the fresh mix and/or for reducing the water content. Superplasticisers are synthetic chemicals consisting of high molecular weight - water soluble polymers. Solubility is ensured by the presence of adequate hydroxyl, sulfonate or carboxylate groups attached to the main organic repeat unit which is usually anionic in nature (Ramachadran, 1996). Different types of superplasticizers are available (Young, 2012), (i) sulfonated melamine, (ii) sulfonated naphthalene formaldehyde, (iii) lignosulfonates, and (iv) polycarboxylates. The latter has been widely used since one decade.

The influence of superplasticizers is assumed to be negligible in most of the applications in civil engineering. However, not much is known about the long-term evolution of cement-bound SP in hardened concrete. Keith-Roach and Höglund (2018) referred in their review some studies where the use SP improve mechanical properties as porosity or reduce the Cl- concentration of cement porewaters, which is beneficial for long-term structural properties of concrete. The same authors also indicated that no significant effect of SP was found on the kind or amount of hydration products or pore solution composition. In addition, in radioactive waste management, the role of superplasticizers with regard to radionuclide complexation with organic molecules motivated a number of studies (Glaus *et al.*, 2003; Young, 2012; Wieland *et al*., 2014; Garcia *et al*., 2018). Regarding the sorption properties of the admixtures on cement-based materials, sorption values remain low compared to that of radionuclide sorption (Glaus *et al*., 2006; Wieland *et al*., 2014).

5.5 Chemical evolution

As described previously, the cement-based materials are in equilibrium at high pH conditions. Consequently, in a natural environment, *i.e.* around pH 7, cement-based materials are chemically unstable. The consequences, in presence of natural waters, are the leaching of selected species into the pore solution such as Na and K, and a gradual dissolution of cement hydrates leading to a degradation of the cement-based materials. This degradation evolves with time, regarding the mineralogical composition. The pH is the main parameter illustrating this degradation process and its evolution is an indicator on the degradation level. A universal description has been adopted for characterizing the chemical evolution of the cement-based materials under disposal conditions (Ochs *et al.*, 2016). This description is based on four degradation stages (I up to IV). Each step is related to the time scale under the assumptions specific for Dessel site and physicochemical processes of some key minerals as follows (Ochs *et al*., 2016):

- <u>Stage I (13.5>pH>12.5, 3 years)</u>: The pristine cement-based materials have a hyperalkaline pore water (pH~13.5). In contact with natural waters, alkalis (Na and K) are gradually removed from the pore volume until very low Na and K concentrations. The lower pH limit (pH=12.5) corresponds to the thermodynamic equilibrium with portlandite in free alkali solution.

- <u>Stage II (pH=12.5, 3,500 years)</u>: the pH of the pore fluid is controlled by the solubility of portlandite. Typically, the pore solution is composed by Ca cations (0.02 mol/kg) and OH^- (0.035 mol/kg). The duration of this step depends on the portlandite content which acts as a buffer.

- <u>Stage III (12.5>pH>10, 36,400 years)</u>: after the complete dissolution of portlandite (state II), the C-S-H phase is gradually decalcified from a C/S ratio of 1.5 down to C/S=0.7. The pore solution is mainly controlled by Ca-concentration which evolves from 0.02 mol/kg down to 0.001 mol/kg; cations are balanced by OH^- ions for high C/S ratios and Si(OH)nx species (n=2,3 and x=-2,-1 respectively) for the lowest C/S ratios.

- <u>Stage IV (10>pH)</u>: Once C-S-H are completely dissolved, calcite (in the presence of carbonate) and silica control the pore fluid chemistry.

FIGURE 5-6 presents a schematic description of the degradation of cement-based materials with the corresponding pH decrease as a function of time and the definition of the degradation stages as described above.

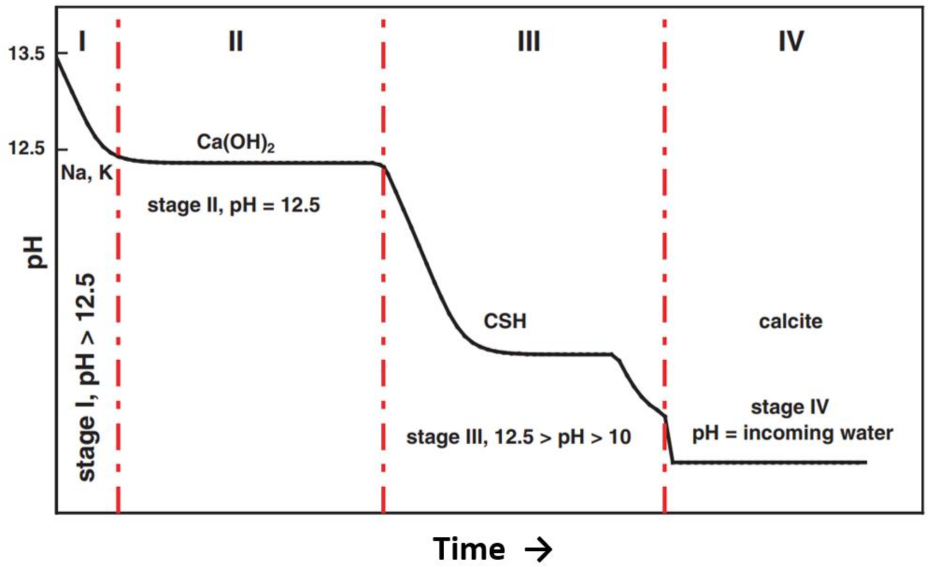

FIGURE 5-6*: Schematic diagram illustrating the evolution of pH associated to the gradual degradation of cement-based materials defining four degradation stages (I to IV) (adj. from Ochs et al., 2016).*

5.6 Effect of the sorption on chemical properties

The sorption of species in solution, or more generally their interactions with the cementitious matrix, depends on the chemical and physical properties of the cement hydrates, mostly C-S-H. This part is not dedicated to a wide overview of radionuclide sorption in cement-based materials (for which one can refer to Evans (2008) and Ochs *et al*. (2016) regarding radionuclide sorption). It rather discusses the role of sorption processes on the chemical equilibrium of the cement hydrates, especially C-S-H. An example of this is the effect of the sorption of alkalis (Na and K) on cement hydrates regarding the composition of the pore solution (Brouwers, 2003). Also, alkali sorption is high for low C/S C-S-H. The amount of cations (Na^+) fixed by C-S-H is then balanced in the solution by calcium ions released by C-S-H increasing the Ca concentration as shown in *FIGURE* 5-7 (Henocq, 2017). As expected, the release of calcium increases as the liquid/solid (L/S) ratio decreases, and consequently, for high concentrations of NaCl (up to 1 M), the Ca concentration can be 30 times higher compared to the free-alkali C-S-H (for L/S=20).

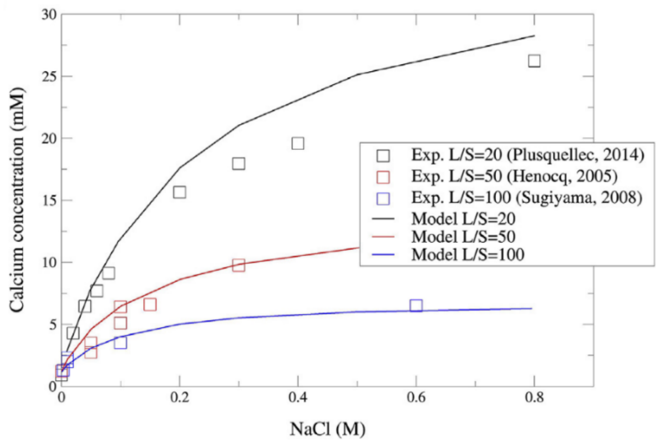

FIGURE 5-7*: Effect of the Na^+ sorption on the chemistry of C-S-H: evolution of the calcium concentration of C-S-H (C/S=0.8) at equilibrium as a function of NaCl concentration with different liquid-to-solid ratios (L/S). Experiments and modelling (Henocq, 2017).*

The cations such as Na^+ species are favourably sorbed on C-S-H with a low C/S ratio. This sorption dramatically falls as the C/S ratio increases (Henocq, 2017). The mechanisms induced in the observations in *FIGURE* 5-7 are minor in the case of the chemical system defined by a pristine hydrated cement paste. However, they would occur in the case of degraded cement-based materials.

5.7 Conclusion

The cement-based materials form a complex chemical system, which is not in equilibrium in most of the cases, especially in the context of a deep geological radioactive waste repository. The cementitious matrix is composed of several minerals, which play a role for the chemical evolution and the related radionuclide sorption processes. There is a good knowledge regarding the cement chemistry and a wide literature dedicated to the various cement types, which allows to characterize their chemical evolution with time and their contribution in terms of sorption.

5.8 References Chapter 5

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