6th IGD-TP Exchange Forum (EF6)

WG3 –Cement Organics Radionuclides Interactions –(CORI)

Topic on: Degradation of Organic Products by Radiolysis/Hydrolysis

London, November 3-4, 2015

J.Vandenborre

Subatech

CORI PROJECT =

1) WP: Degradation of Organic Products by Radiolysis/Hydrolysis

Why ? : Degradation mechanisms of OP insufficiently known in literature for high pH (> 12)

Key Topic : Kinetic Study of Degradation Rates by Radiolysis/Hydrolysis

Aim : Database of Relevant Organic Products as Source Term which can be used in other WPs

2) WP: Mobility of Organics in Cementitious Environment and their Interaction with Fe

3) WP : Mobility of Organics-RN Complexes in a Cementitious Environment

4) WP : Modelling, Upscaling, Application to PA

WG3-CORI: WP « Degradation of Organic Products by Radiolysis/Hydrolysis »

PARTNERS

Consortia for

Irradiation Tools

→ Parallel Experiments

between Hydrolytic

and Radiolytic

Degradations

WMO

Interested

SUBATECH
AMPHOS21
FZJUELICH
KIT-INE
PSI
CEA ?
SCK-CEN
UPPC
Manchester University
ANDRA
ONDRAF
SKB

WG3-CORI: WP « Degradation of Organic Products by Radiolysis/Hydrolysis »

Laboratory	SUBATECH	AMPHOS21	FZJULICH	KIT-INE	PSI	SCK-CEN	UPPC	Manch.Univ
Radiation	√		√	√		√		√
Polycarboxylate as Superpasticiz	√	√		√			√	
Phtalate as Superpasticiz			√	√			√	√
PVC as Plastic		√	√		√			√
Ion. Exch Resins	√	√	√		√	√	√	√
Carboxylic Acid as simpl molec	√				√	√	√	
Cellulose, ISA		√		√		√		√
CSH Phase	√		√	√		√	√	√
CEM (III-V) phase		√	√			√		
Portland Phase	√	√	√	√	√	√	√	√
Analytic Tools for Organic molecules in solution	UV-VIS, HPLC, GC-MS, ICP-MS, Ion Chromatog COT, LC-MS, ESR	TRLFS, UV-VIS, ICP-MS, ICP-OES, TOC, Ionic Chromatography, CE, ESI-MS	GC-MS, HPLC-MS, IC/CE/LC-MS, ICP-MS, NMR	TRLFS, LSC, ICP-MS, TOC, UV-vis,	Ion exclusion chromatography, + Mass Spectrometry , TOC	UV-Vis, FT-IR, HPLC/SEC, HPLC-MS, ICP-AES, ICP-MS, TOC/IC,	Luminescence/ Fluorescence spectroscopy, Raman spectroscopy	IR, ICP AES, -MS, HPLC-ICP-MS, GCMS, LCMS
For Gas measurements	µGC, IR		GC-MS		GC+MS	µGC; GC-FID		
Rates Det. Modelling	Maksima Chemsimul		CHEMSIMUL Molecular Dynamics	MCNP calculations		COMSOL pFLOTRAN Phreeqc		
Other WPs Implication	√√	√√	√√	√√	√	√√	√	√

OP Degradation Rates Determination :

- Kinetic Studies vs. Time (Irradiation or Chemical)
- Hydrolytic Degradation Experiments : Experimental Conditions

pH = 12.5, Aerated/Anoxic Atmosphere, With/Without Initial H_2 gas, With/Without Cement Phases, Temperature ?

- Radiolytic Degradation Experiments (Same Conditions)

Irradiation Tools/Facilities Available (γ and He^{2+} for α emitter)

5 Partners (5 γ-sources, 1 α doping and 1 cyclotron facility)

Consortia for parallel experiments between hydrolitic and radiolytic degradation

WG3-CORI: WP « Degradation of Organic Products by Radiolysis/Hydrolysis »

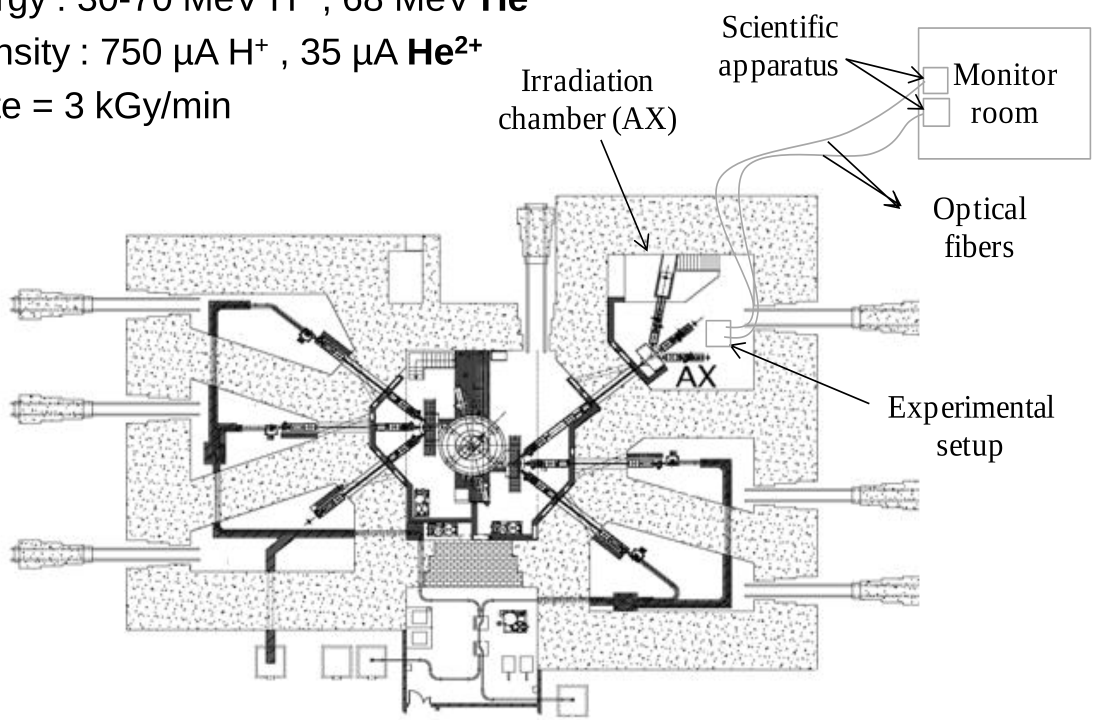
Cyclotron Facility = External Source

Bi-particles : H^+ / **He^{2+}**

High energy : 30-70 MeV H^+ , 68 MeV **He^{2+}**

High intensity : 750 µA H^+ , 35 µA **He^{2+}**

Dose Rate = 3 kGy/min



Large range of Dose Rate

(^{137}Cs-^{60}Co)

= 60 Gy/h – 10 kGy/h

α Doping = Internal Source

Complementary radiolytic degradation experiments

Tandem 15 MeV He^{2+} / 10 MeV H^+

WG3-CORI: WP « Degradation of Organic Products by Radiolysis/Hydrolysis »

Laboratory	SUBATECH	AMPHOS21	FZJULICH	KIT-INE	PSI	SCK-CEN	UPPC	Manch.Univ
Radiation	√		√	√		√		√
Polycarboxylate as Superpasticiz	√	√		√			√	
Phtalate as Superpasticiz			√	√			√	√
PVC as Plastic		√	√		√			√
Ion. Exch Resins	√	√	√		√	√	√	√
Carboxylic Acid as simpl molec	√				√	√	√	
Cellulose, ISA		√		√		√		√
CSH Phase	√		√	√		√	√	√
CEM (III-V) phase		√	√			√		
Portland Phase	√	√	√	√	√	√	√	√
Analytic Tools for Organic molecules in solution	UV-VIS, HPLC, GC-MS, ICP-MS, Ion Chromatog COT, LC-MS, ESR	TRLFS, UV-VIS, ICP-MS, ICP-OES, TOC, Ionic Chromatography, CE, ESI-MS	GC-MS, HPLC-MS, IC/CE/LC-MS, ICP-MS, NMR	TRLFS, LSC, ICP-MS, TOC, UV-vis,	Ion exclusion chromatography, + Mass Spectrometry, TOC	UV-Vis, FT-IR, HPLC/SEC, HPLC-MS, ICP-AES, ICP-MS, TOC/IC,	Luminescence/ Fluorescence spectroscopy, Raman spectroscopy	IR, ICP AES, -MS, HPLC-ICP-MS, GCMS, LCMS
For Gas measurements	µGC, IR		GC-MS		GC+MS	µGC; GC-FID		
Rates Det. Modelling	Maksima Chemsimul		CHEMSIMUL Molecular Dynamics	MCNP calculations		COMSOL pFLOTRAN Phreeqc		
Other WPs Implication	√√	√√	√√	√√	√	√√	√	√

Organic Products selected:

Representative Organic Ligands in Nuclear Waste Management

+ Degradation Products from these ROL (Simple Molecule)

1) PVC as Plastics

2) Cellulose

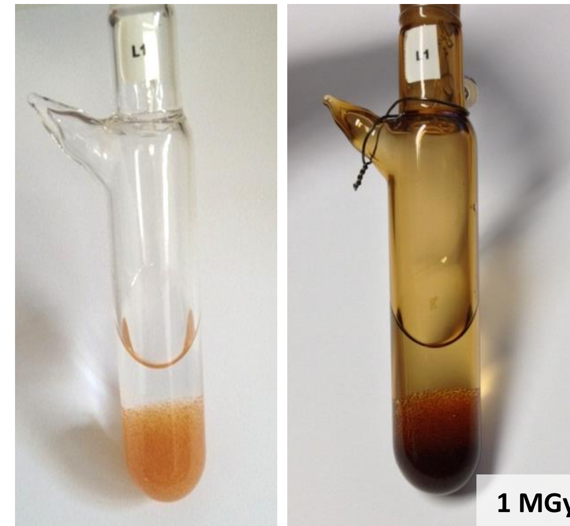
3) Phtalate/Polycarboxylate as Superplasticiser (commercial SP ?)

4) Ionic Exchange Resins

5) Low Molecular Weight Organics (Carboxylic Acid: Formic / Acetic / Oxalic ; ISA…) considered as degradation products from 1-2-3-4 groups

Examples of JUELICH for CORI WP2 (I)

I. Radiolytic degradation of spent ion exchange resins (SIER)



- Investigated materials:
  - IERs
  - model substances (polymers) to simulate radiolysis of different functional groups
- Co-60 γ-irradiation up to 10 MGy
- controlled aerobic/anaerobic conditions
- different solution compositions
- Analytical approach:
  - Gas phase: GC →: G-values, speciation
  - Liquid phase: HPLC, LSC, ^{1}H-NMR → total released fraction, ^{14}C-speciation
  - Solid phase (IERs): SS-NMR, FTIR, RAMAN → final structure

➢ Results:

➢ Different organic species in the gas phase varying with dose

Dose →

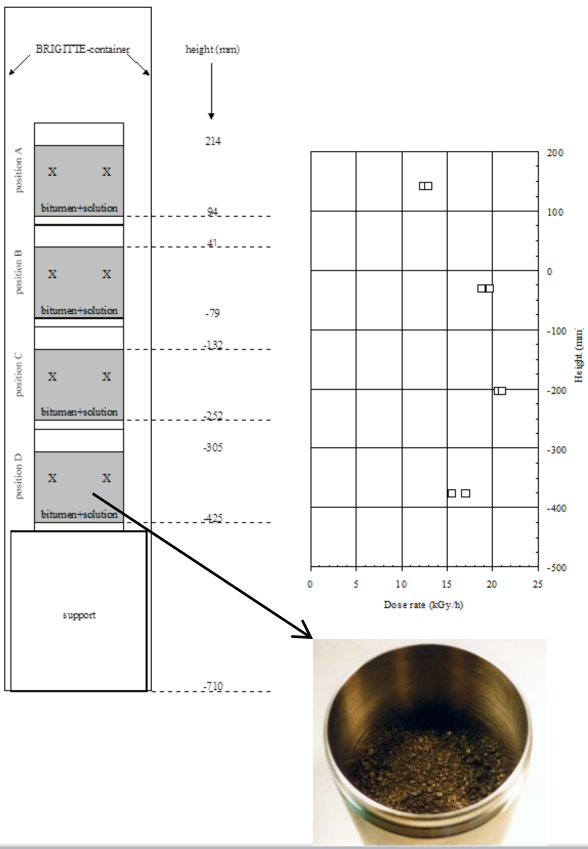
($(CH_3)N$; $HCOH$; $H_2C=CH_2$; $H_3C\text{-}COH$)

➢ Formic acid in the aqueous phase

➢ Quantitative analysis of released species

Characterisation of chemical and radiolytic degrad. prod. of Eurobitum

- Inactive Eurobitum in contact with artificial Boom Clay water (SCW) or cement-equilibrated water (CCW), without DOM, gamma-irradiated until 4.8 MGy
- A.o. IC-EC and GC-MS of degradation product solution



	SCW		CCW	
(Concentration in mg/L)	**irradiated**	**control**	**irradiated**	**control**
total DOC before treatment	< 9	< 9	6.3 (1.4)	6.3 (1.4)
total DOC after treatment	769 (91)	39 (6)	962 (110)	77 (8)
formate	127 (13)	7 (2)	129 (13)	n.m.
acetate	319 (32)	< 10	393 (39)	n.m.
oxalate	59 (15)	< 10	184 (18)	n.m.

WG3-CORI: WP « Degradation of Organic Products by Radiolysis/Hydrolysis »

Laboratory	SUBATECH	AMPHOS21	FZJULICH	KIT-INE	PSI	SCK-CEN	UPPC	Manch.Univ
Radiation	√		√	√		√		√
Polycarboxylate as Superpasticiz	√	√		√			√	
Phtalate as Superpasticiz			√	√			√	√
PVC as Plastic		√	√		√			√
Ion. Exch Resins	√	√	√		√	√	√	√
Carboxylic Acid as simpl molec	√				√	√	√	
Cellulose, ISA		√		√		√		√
CSH Phase	√		√	√		√	√	√
CEM (III-V) phase		√	√			√		
Portland Phase	√	√	√	√	√	√	√	√
Analytic Tools for Organic molecules in solution	UV-VIS, HPLC, GC-MS, ICP-MS, Ion Chromatog COT, LC-MS, ESR	TRLFS, UV-VIS, ICP-MS, ICP-OES, TOC, Ionic Chromatography, CE, ESI-MS	GC-MS, HPLC-MS, IC/CE/LC-MS, ICP-MS, NMR	TRLFS, LSC, ICP-MS, TOC, UV-vis,	Ion exclusion chromatography, + Mass Spectrometry, TOC	UV-Vis, FT-IR, HPLC/SEC, HPLC-MS, ICP-AES, ICP-MS, TOC/IC,	Luminescence/ Fluorescence spectroscopy, Raman spectroscopy	IR, ICP AES, -MS, HPLC-ICP-MS, GCMS, LCMS
For Gas measurements	µGC, IR		GC-MS		GC+MS	µGC; GC-FID		
Rates Det. Modelling	Maksima Chemsimul		CHEMSIMUL Molecular Dynamics	MCNP calculations		COMSOL pFLOTRAN Phreeqc		
Other WPs Implication	√√	√√	√√	√√	√	√√	√	√

Solids Addition :

Impact of the solid onto degradation rates?

+ Impact of the Radiolytic/Hydrolytic Degradation processes onto the solid?

1) Cement Phase : CSH = Calcium-Silica-Hydrate = Simplest Phase (C/S Ratio?)
2) Initial CEM (before Degradation)

CEM I = Ordinary Portland

Other Blended Cements CEM (III-V) = more complex ?

3) Degraded CEM Analysis during/after degradation experiments

Carbonated Cement ?

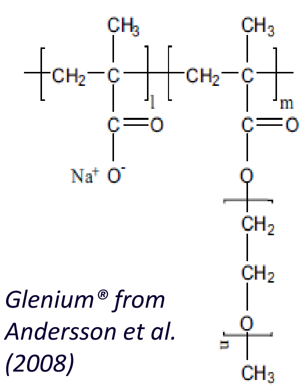
Degradation of Organics products by hydrolysis/radiolysis

Amphos 21 interests:

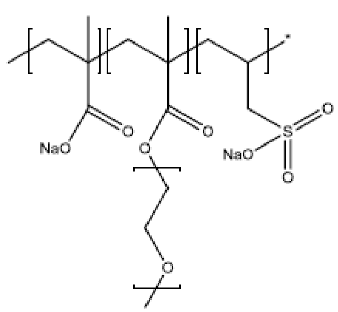
- Study of the degradation of organic additives (superplasticizers, SPs) by radiolysis prior to their incorporation into the concrete.
- Study whether the degradation of those organics additives once incorporated in the cementitious material, harden cement paste (HCP) radiolysis.

OP studied

- Commercial product, Glenium SPs (PCE based SPs)
- SPs proxy based on a PCE SPs



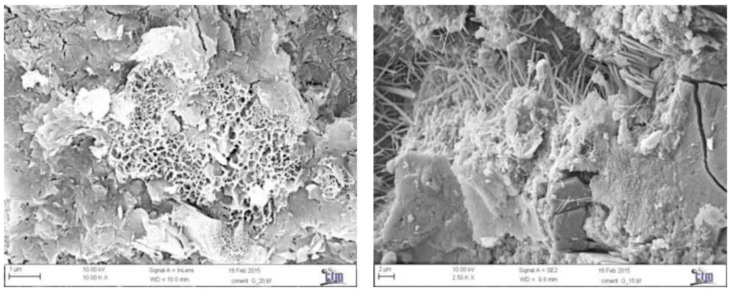
Glenium® from Andersson et al. (2008)



PCE based SPs from Isaacs PhD. Thesis (2015)

CEM phase

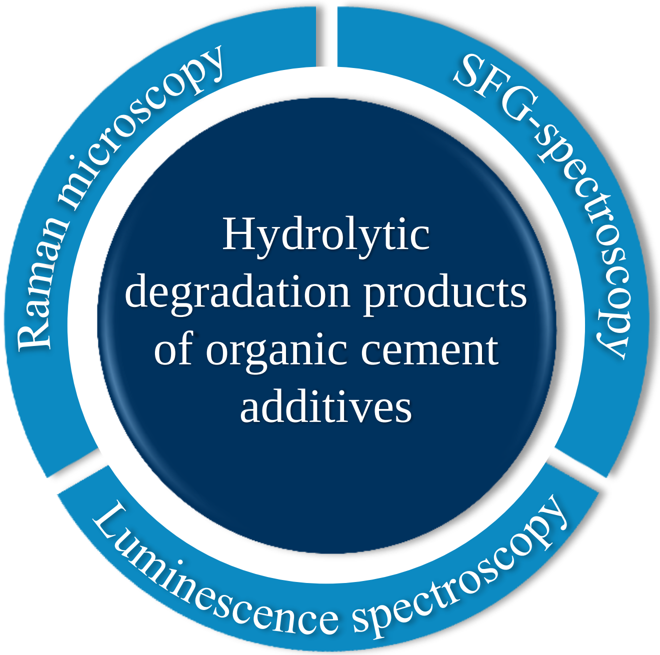
- Two types of Hardened Cement Paste (HCP)
  - Based on CEM I
  - Based on CEM V



From García et al. (2015)

1994-2014 20 YEARS FLOWING

Analytical tools and substances to be investigated



- Site-selective spectroscopy at ultra low-temperatures
- Time-resolved and steady-state fluorescence spectroscopy
- Stop-flow experiments
- Interlanthanide energy transfer

- *Organic products*:
  - Polycarboxylates
  - Phthalates
  - Ionic exchange resins
  - Low molecular weight organic acids (C2 – C10)
- *Radionuclides (Ln(III) as analogs) and system components*:
  - Ln(III) (especially Eu(III))
  - Fe(II) / Fe(III)
  - SO_4^{2-}/S^{2-}
  - Ca(II)
  - U(VI) (if provided by partner)
- *Cement phases*:
  - CSH (reference: ettringite, tobermorite)
  - Portland (e. g. alite, belite)

WG3-CORI: WP « Degradation of Organic Products by Radiolysis/Hydrolysis »

Laboratory	SUBATECH	AMPHOS21	FZJULICH	KIT-INE	PSI	SCK-CEN	UPPC	Manch.Univ
Radiation	√		√	√		√		√
Polycarboxylate as Superpasticiz	√	√		√			√	
Phtalate as Superpasticiz			√	√			√	√
PVC as Plastic		√	√		√			√
Ion. Exch Resins	√	√	√		√	√	√	√
Carboxylic Acid as simpl molec	√				√	√	√	
Cellulose, ISA		√		√		√		√
CSH Phase	√		√	√		√	√	√
CEM (III-V) phase		√	√			√		
Portland Phase	√	√	√	√	√	√	√	√
Analytic Tools for Organic molecules in solution	UV-VIS, HPLC, GC-MS, ICP-MS, Ion Chromatog COT, LC-MS, ESR	TRLFS, UV-VIS, ICP-MS, ICP-OES, TOC, Ionic Chromatography, CE, ESI-MS	GC-MS, HPLC-MS, IC/CE/LC-MS, ICP-MS, NMR	TRLFS, LSC, ICP-MS, TOC, UV-vis,	Ion exclusion chromatography, + Mass Spectrometry, TOC	UV-Vis, FT-IR, HPLC/SEC, HPLC-MS, ICP-AES, ICP-MS, TOC/IC,	Luminescence/ Fluorescence spectroscopy, Raman spectroscopy	IR, ICP AES, -MS, HPLC-ICP-MS, GCMS, LCMS
For Gas measurements	µGC, IR		GC-MS		GC+MS	µGC; GC-FID		
Rates Det. Modelling	Maksima Chemsimul		CHEMSIMUL Molecular Dynamics	MCNP calculations		COMSOL pFLOTRAN Phreeqc		
Other WPs Implication	√√	√√	√√	√√	√	√√	√	√

Complementary Approach : Solution + Gas + Solid

Solution : Simple molecules (C-Species) detection + quantification

1) Mass Spectroscopies (GC, ICP, LC, ESI)

2) Liquid (HPLC, Ionic Chromatography, TOC)

3) UV-VIS Speciation (*in situ* = during experiment)

Solid : Surface Phase Characterization during/after experiments

1) Fluorescence/Luminescence Spectroscopies (Time-Resolved-LFS)

2) Vibrationnal Spectroscopies (FT-IR, Raman)

3) X-Ray Diffraction, SEM-EDX, XPS, AFM

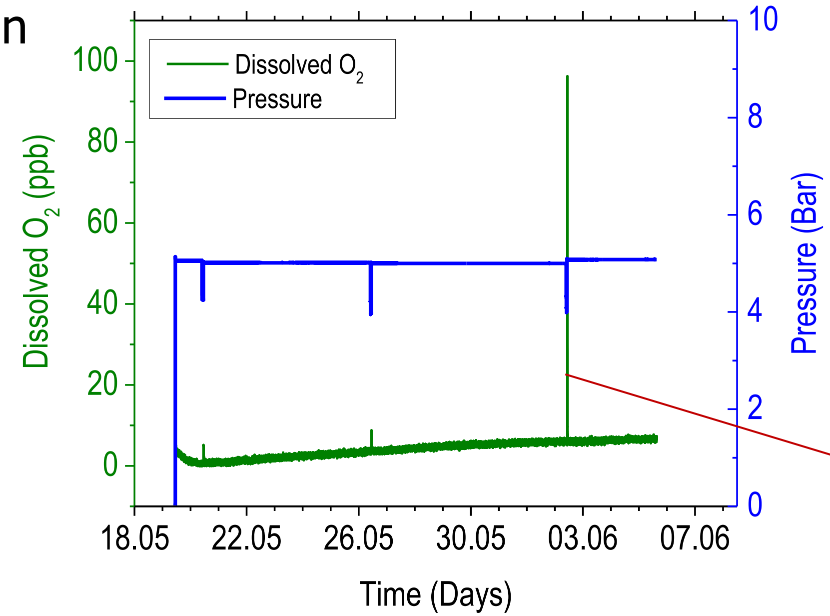
Gas : Radiolytic Production (H_2, C_xH_y, CO, CO_2...) to determine yields

1) Gas Chromatography (+MS, +FID), 2) IR

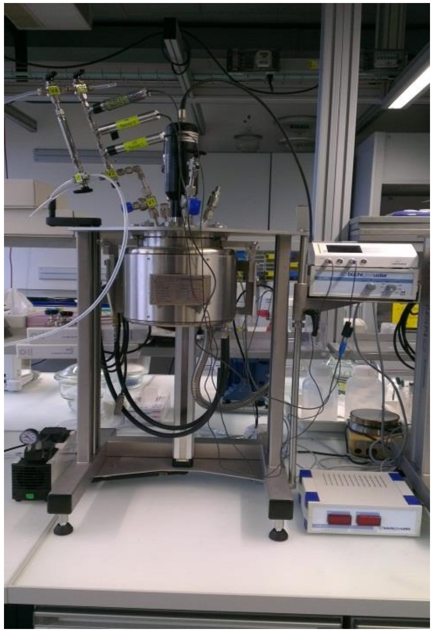
Degradation of organics under repository relevant conditions

❑ Reactor system

- Set-up of the gas-tight reactor system including monitoring of:
  - pressure
  - O_2 concentration
  - temperature



Sampling + re-adjustment of liquid volume with O_2 saturated Milli-Q water



❑ Analytical tools

- Identification of the degradation products
  - i) in the liquid phase using high performance ion exclusion chromatography with mass spectrometry
  - ii) in gas phase using gas chromatography with mass spectrometry
- Determination of total and organic carbon contents

WG3-CORI: WP « Degradation of Organic Products by Radiolysis/Hydrolysis »

Laboratory	SUBATECH	AMPHOS21	FZJULICH	KIT-INE	PSI	SCK-CEN	UPPC	Manch.Univ
Radiation	√		√	√		√		√
Polycarboxylate as Superpasticiz	√	√		√			√	
Phtalate as Superpasticiz			√	√			√	√
PVC as Plastic		√	√		√			√
Ion. Exch Resins	√	√	√		√	√	√	√
Carboxylic Acid as simpl molec	√				√	√	√	
Cellulose, ISA		√		√		√		√
CSH Phase	√		√	√		√	√	√
CEM (III-V) phase		√	√			√		
Portland Phase	√	√	√	√	√	√	√	√
Analytic Tools for Organic molecules in solution	UV-VIS, HPLC, GC-MS, ICP-MS, Ion Chromatog COT, LC-MS, ESR	TRLFS, UV-VIS, ICP-MS, ICP-OES, TOC, Ionic Chromatography , CE, ESI-MS	GC-MS, HPLC-MS, IC/CE/LC-MS, ICP-MS, NMR	TRLFS, LSC, ICP-MS, TOC, UV-vis,	Ion exclusion chromatography, + Mass Spectrometry , TOC	UV-Vis, FT-IR, HPLC/SEC, HPLC-MS, ICP-AES, ICP-MS, TOC/IC,	Luminescence/ Fluorescence spectroscopy, Raman spectroscopy	IR, ICP AES, -MS, HPLC-ICP-MS, GCMS, LCMS
For Gas measurements	µGC, IR		GC-MS		GC+MS	µGC; GC-FID		
Rates Det. Modelling	Maksima Chemsimul		CHEMSIMUL Molecular Dynamics	MCNP calculations		COMSOL pFLOTRAN Phreeqc		
Other WPs	√√	√√	√√	√√	√	√√	√	√

OP Degradation Rates Determination Modelling:

From Experimental Data obtained in the WP

Modelling to extrapolate Degradation Rates Determination vs.:

Degradation Time, Dose, Dose Rate, Temperature….

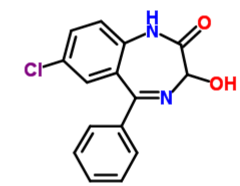
Strong Overlap with WP "Modelling, Upscaling, Application to PA"

Hydrolytic/Radiolytic OP Degradation Rates Database (Source Term):

Strong Overlap with WP "Mobility of Organics in Cementitious Environment and their Interaction with Fe"

Link with WP « Modelling »

Degradation analysis and modeling (PhreeqC)



- **Oxazepam degradation**
  - *Degradation rate*: First-order kinetic

$$\frac{\partial C_{water}}{\partial t} = -k_{deg} \cdot C_{water}$$

  - *Sorption:* DLM for hydrophobic surfaces ; constants predicted using QSAR (Chemaxxon + Franco and Trapp 2008)
  - *Evolution of the surface properties*:

$$\frac{\partial C_{water}}{\partial t} = -(k_{ads} \cdot C_{water} - k_{des} \cdot C_{sediment})$$

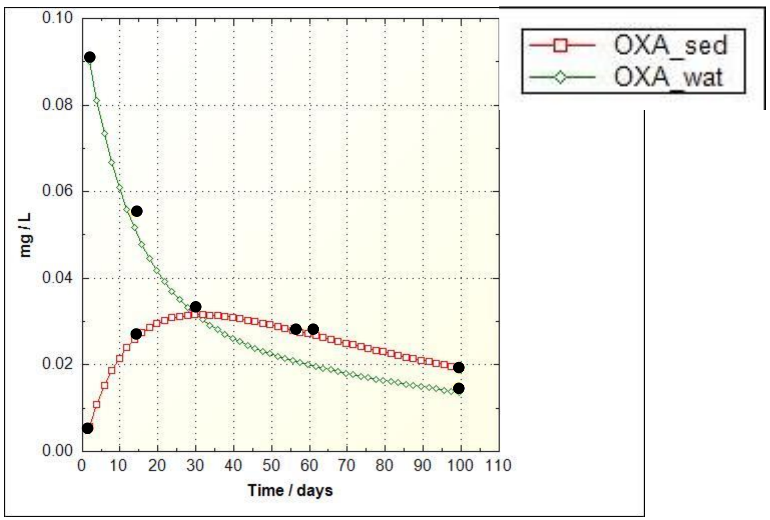
  - *Aqueous complexation*: pKa from QSAR modeling (ACD Labs)

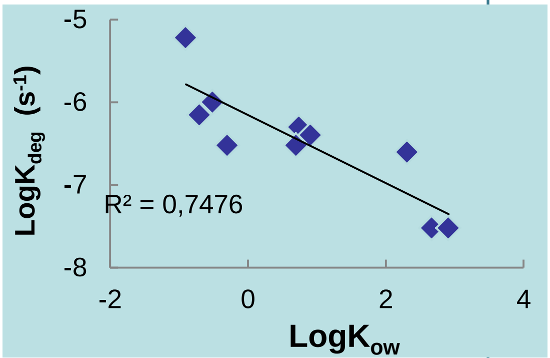
Löffler et al. (2005)

Sediment TOC 1.4%

L/S = 5 ;
pH = 8.5

$LogK_{ow}$ = 2.9
pKa = 10.7
$LogK_{oc}$ = 2.2





Generalization for hydrophylic to slightly hydrophobic molecules

brgm Géosciences pour une Terre durable

WG3-CORI: WP « Degradation of Organic Products by Radiolysis/Hydrolysis »

OP ± Cement Phases

Organic Products
1) PVC
2) Cellulose
3) Phtalate/Polycarboxylate
4) Ionic Exchange Resins
5) LMWO as deg. products

With/Without

Cement Phases
1) CSH
2) CEM I = Portland
3) CEM III-V

WMO

Degradation Experiments

pH = 12.5
Atmosphere : Anoxic/Aerated
± Initial H_2g
Temperature ?

Hydrolytic

Parallel AND Complementary Experiments

Radiolytic

Irradiation Tools (5γ/1α int.+ext.)

Output: Degradation Rates

By Analytic Tools :
Solution
+ Solid
+ Gas

Modelling

WP Modelling

WPs Mobilities