6th IGD-TP Exchange Forum (EF6) WG3: Cement Organics Radionuclides Interactions (CORI)

WP2:Topic on “Mobility of organics in cementitious environment and their interaction with Fe”

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London, November 3-4, 2015

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Technical/Scientific Working Group (TSWG) : CORI

- TSWG established to discuss relevant issues in the context of Cement-Organics-Radionuclide-Interactions
- **Main objective → to improve the understanding on the behaviour of anthropogenic organic molecules (released from technological wastes, ionic exchange resins and graphite) within cementitious systems.**

- **Identified key-topics**

1. WP1: “Degradation of organics - result of hydrolysis and radiolysis”
2. WP2: “Mobility of organics in cementitious environment and their interaction with Fe”
3. WP3: “Mobility of organics-RN complexes in a cementitious environment”
4. WP4: “Modelling, upscaling, application to PA”

Additional WPs on Management (Coord. KIT) + Training/Dissemination

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WP2: Mobility of organics in cementitious environment and their interaction with Fe

WP2 constitutes a link between the WP1 dealing with source term & kinetics release **and the WP3** focused on the direct consequences onto RN mobility

WP1

Degradation of organics
=> Result of hydrolysis and radiolysis

WP2

Mobility of organics in cementitious environment and their interaction with Fe

WP3

Mobility of organics-RN complexes in a cementitious environment

WP4

Modelling, upscaling, application to PA

WP1, WP2 and WP3 provide input for **WP4**

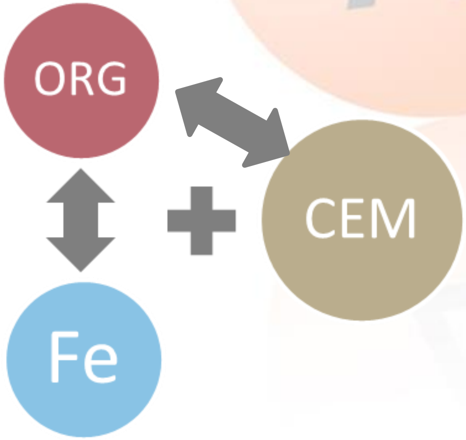
WP2: Mobility of organics in cementitious environment and their interaction with Fe

Objectives

- **Competitive effect of organic ligands** on both

sorption onto cement phases

Fe complexation in ternary systems Fe-ORG-CEM



- Although Kd values for different organic molecules are available, **further understanding of sorption mechanisms is still necessary**:

WHY??

i. Evaluate the **reversibility and long-time effects** on organic sorption.
ii. Study the **effect of cement degradation** on organic sorption.
iii. Understand the **competition effect** among the different organic molecules for cement sorption sites.
iv. Investigate the **effect of significant iron amounts** on the system and how its presence can affect ORG organic sorption onto cement and complexation capacity of organics with RN **(link with CORI WP3** *"Mobility of organics-RN complexes in a cementitious*

Tentative Organizations/WMO showing interest in WP2

14 Organisations/Research Institutes and Universities

Subatech
cea
UNIVERSITÄT BERN
SCK•CEN
STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE
KIT Karlsruher Institut für Technologie
The University Of Sheffield.
JÜLICH FORSCHUNGSZENTRUM
JG|U JOHANNES GUTENBERG UNIVERSITÄT MAINZ
Universität Potsdam
AMPHOS 21 SCIENTIFIC AND STRATEGIC ENVIRONMENTAL CONSULTING
MANCHESTER 1824 The University of Manchester
TERAMED s.r.o.
ČESKÉ VYSOKÉ UČENÍ TECHNICKÉ V PRAZE
UNIVERSITÄT HEIDELBERG ZUKUNFT SEIT 1386

5 WMO

ANDRA French national radioactive waste management agency
SKB
ONDRAF/NIRAS
Radioactive Waste Management
nagra.

Summary of info received from the different organizations

Organization	Type of Organicsː SPL	Plastics	Resins	Bitumen	Simple ORG	Other	Dissolved org. species considered as ligands (in orange the organics proposed in this presentation and common to all the organizations)
ANDRA	✓	✓	✓	✓	✓	✓	acetic, adipic, benzoic, formic, gluconic, glutaric, ISA, lactic, malonic, oxalic, phthalic, pimelic, sorbic, succinic. TBP, EDTA, DTPA, NTA, polycarboxylates.
SKB	✓	✓	✓	✗	✓	✓	NTA, ISA, Polyacrylonitrile polymers
ONDRAF/NIRAS	✓	✓	✓	✗	✓	✓	Phthalates, polystyrene (divinyldibenzene); mixture styrene and vinyl ester, EDTA, ISA…
NAGRA	✓	✓	✓	✓	✗	✗	GLU, ISA, CN, EDTA
RWM	✓	✓	✓	✗	✓	✓	ISA, CDP, polycarboxylates, EDTA, NTA, DTPA, TBP, phtalate
CEA	✓	✓	✓	✓	✓	✓	ISA, phthalic, adipic. EDTA and gluconic acid as secondary priority.
AMPHOS	✓	✓	✓	✓	✓	✓	ISA, benzoic, oxalic, formic, acetic, malonic, phthalic, adipic,succinic, sorbic
SUBATECH	✓	✓	✓	✓	✓	✓	Gluconate, polycarboxylate, C-14 Radiolabelled PCs, NOM (humic acids)
U. BERN	✗	✓	✓	✗	✓	✗	Mainly C14-bearing organic compounds: Alkanes, Carboxyl acids, Alcohols , Aldehydes, ISA, polyhydroxycarboxylates, metal (Fe) organic complexes.
SCK/CEN	✓	✓	✓	✓	✓	✗	NOM, Acetate, formate, oxalate, ISA; tartaric acid, galacturonic acid, …
KIT-INE	✓	✓	✓	✓	✓	✓	ISA, gluconate, phthalate, cellulose degradation mix (from WP2)
U. SHEFFIELD	✓	✓	✗	✗	✓	✓	Small organic acids and polycarboxylates
U. HEIDELBERG	✓	✗	✗	✗	✓	✗	Polycarboxylates (Model ligands for Plasticizer and Superplasticizer)
U. PRAGUE	✗	✓	✗	✗	✓	✗	Extractants (DGAs, crown ethers, macrocycles, GO…) , Ion exchangers/ extraction resins degradation products, humic substances. ISA, EDTA, oxalic acid, isocyanate
JUELICH	✓	✓	✓	✗	✗	✓	Oxalate, phthalate, amines & IER-degradation products
TERAMED	✗	✗	✗	✗	✓	✓	VFA, acetates, organic acids, polymeric compounds and humic acid fragments
U.POTSDAM	✓	✓	✓	✓	✓	✗	(polycyclic) aromatic hydrocarbons, Bis(triazinyl)pyridine, Bis(triphenyl)bipyridine, Bis(chlorophenyl)-dithiophosphonic acid, SNF, Lignosulphonates.
U. MANCHESTER	✓	✓	✓	✓	✓	✓	Phthalate, ISA, gluconate, cellulos microbial degradation, platics microbial degradation, etc…

Summary of info received from the different organizations

Organization	Type of cement/phase					CEM Deg.
	CEM I	CEM II / III / IV / V	C-S-H/ CASH	AFt / AFm	Other(fly-ash, NRVB, ...)	
ANDRA	✓	✓	✗	✗	✗	Hydrolysis, Carbonation
SKB	✓	✗	✗	✗	✗	Hydrolysis, Carbonation
ONDRAF/NIRAS	✓	✓	✗	✗	✗	✓
NAGRA	✓	✗	✗	✗	✗	✓
RWM					✓	✓
CEA	✗	✓	✗	✗	✗	State I, II, III and carbonated
AMPHOS	✓	✓	✓	✗	✗	State I, II, III and carbonated
SUBATECH	✓	✗	✓	✓	✓	Different C/S ratios for C-S-H
U. BERN	✗	✗	✓	✓	✗	✗
SCK/CEN	✓	✗	✗	✗	✗	State I, II, III and carbonated
KIT-INE	✓	✗	✓	✓	✗	10.0 ≤ pH ≤ 13.3
U. SHEFFIELD	✗	✓	✗	✗	✓	Leaching, Rad., Ageing, Thermal proc.
U. HEIDELBERG	✗	✗	✗	✗	✗	✗
U. PRAGUE	✓	✓	✗	✗	✗	✓
JUELICH	✓	✓	✓	✓	✓	✗
TERAMED	✗	✓	✗	✗	✓	biological degradation, mechanical damage
U. POTSDAM	✓	✓	✗	✗	✗	alteration of cement (formation of CSH phase; Fe corrosion related phases)
U. MANCHESTER	✗	✗	✓	✗	✓	Carbonation, C(A)SH, calcite, Fe-corrosion products

Scope of work   Definition of representative organics

According to the info received from each institution/center, ***a tentative*** selection of **representative organic ligands** is proposed by assuming the following criteria (to be agreed and discussed with WMO):

1. ***Organic waste inventories (according to WMO)***
   Linked to CORI WP1 *(Degradation of organics => Result of hydrolysis and radiolysis),* the study could be limited to **polyacrylates, resins (high amounts), cellulose (polyethylene/polypropylene as option?)** as the main organic wastes found in the repositories. In addition, **superplasticizers** could be included as their use is of utmost importance in cement formulation with non-negligible mass quantity.

2. ***Complexing properties***
   Generic order of organic ligands according to RN complexing capacity in alkaline media
   (link to CORI WP3 *"Mobility of organics-RN complexes in a cementitious environment"***)**

3. ***^{14}C-bearing organic compounds***
   ^{14}C behaviour is directly correlated with its speciation in gaseous and aqueous species. One third of the ^{14}C is considered dissolved organic fraction. Sources of ^{14}C are graphite, end and hulls, ionic exchange resins.

which is the selection of **representative organic ligands proposed? And why?**

See next slides

WP2. Scope of work Definition of representative organics

According to the info received from each institution/center, ***a tentative*** selection of **representative organic ligands** is proposed by assuming the following criteria (to be agreed and discussed with WMO):

1. ***Organic waste inventories***
2. *Complexing properties*
3. *^{14}C-bearing organic compounds*

Organics in wastes	Subgroup	Main degradation product/s
Cement additives (Superplasticiser)	PCE/CAE	Carboxylates
Plastics	PUR, PVC, Polyacrilate, Polyethylene/Polypropylene and degradation products. **Linked to WP1 on degradation of organic's results**	Adipic, Phthalic, Butyric, Succinic, Crotonic, Acetic, Isocyanate
Resins	Cationic and Anionic resins	Oxalic
Bitumen	-	Formic, Acetic, Oxalic
Simple organics (cleaning/extraction agents)	-	EDTA, NTA, DTPA, TBP, DBP
Other	Cellulose and degradation products	ISA

Scope of work Definition of representative organics

According to the info received from each institution/center, ***a tentative*** selection of **representative organic ligands** is proposed by assuming the following criteria (to be agreed and discussed with WMO):

1. *Organic waste inventories*
2. ***Complexing properties***
3. *^{14}C-bearing organic compounds*

Generic order of organic ligands according to RN complexing capacity in alkaline media

ISA (and gluconate) > DTPA > EDTA > NTA > oxalate = malonate = glutarate = succinate > phtalate > adipate > acetate >> formiate

Is it the same order with respect to complexation with Fe

Main focus on ISA regarding complexing properties?

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Scope of work — Definition of representative organics

According to the info received from each institution/center, ***a tentative*** selection of **representative organic ligands** is proposed by assuming the following criteria (to be agreed and discussed with WMO):

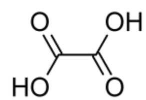
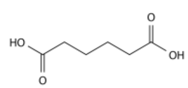
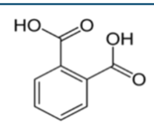
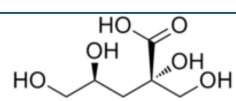
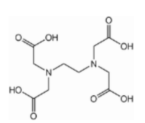
1. *Organic waste inventories*
2. *Complexing properties*
3. ***^{14}C-bearing organic compounds***

Based on inputs from the CAST European project results, this WP within CORI project might provide specific insights on ^{14}C behaviour interaction with cement-based materials

Chemical speciation and concentrations of ^{14}C from irradiated materials ***=> Synergy with CORI WP1.***

Scope of work

From the previous reasoning and slides, the following organic ligands could be proposed to be studied although other molecules could be envisaged according to the WMO’s and other European project inputs:

Organic	Structure	Subgroup	Representation	Analogies
acids/alcohols and/or aldehydes C1-C2		Cationic and Anionic resins/ 14C-bearing organic compounds	Short-chained acids, alcohols and /or aldehydes	Malonic, Succinic…
Adipic acid		PVC/PUR	Long-chained dicarboxylic acid	Glutaric, Pimelic, Suberic…
Phthalic acid		PVC	Aromatic dicarboxylic acid	Succinic
ISA		Cellulosic wastes	Hydroxicarboxylic acid	Citric, gluconic
Acetic	$R\text{-}COO^-$	PCE/CAE	Mono(poly)carboxylic acid	Formic, Butyric, Acetic
EDTA		Decontamination and cleaning	Aminocarboxylic acid	DTPA, NTA

Scope of work

Cementitious environment

Bottom-up approach: From cement phases to actual cementitious systems.

Cement phases

- C-S-H, CASH, Ettringite, Monosulphate…

CEM formulation

- CEM I, CEM II, CEM III, CEM IV, CEM V…

Degraded CEM

1. State I, fresh cement,
2. State II, equilibrium with Portlandite
3. State III, equilibrium with CSH
4. Degraded/Carbonated cement

Structural systems

- Systems including aggregates, Armoured systems…

Scope of work

Influence of iron

Special interest in the role of Fe: special focus on the influence of steel content and of Fe-bearing cement phases as the **main sources or Fe in deep disposal repositories**:

- **Cement**. More specifically from Ferrite (Ca_2AlFeO_5). This phase makes up 5-15% of normal Portland cement clinkers.

- **Steel armoured system as significant Fe source** : between 4 and 7% of the total mass of concrete canisters, Fe/cement mass ratio between 0.15-0.20, as illustration.
  - **Oxic conditions**, Fe^0 is kinetically corroded and **goethite** can be formed
  - **Anoxic/reducing conditions**, **Magnetite** precipitation (this phase is in chemical equilibrium with the pore water).

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Bottom-up approach and modelling

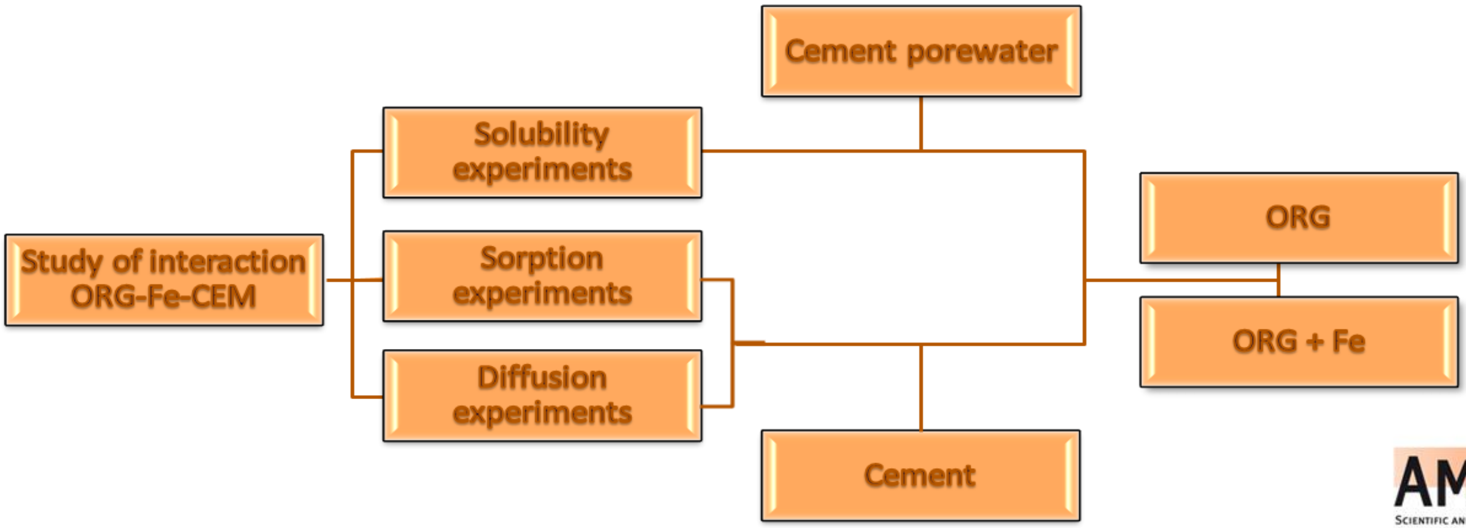
Bottom-up approach

Generic and systematic approaches should be designed in this frame. **Each laboratory input (capabilities, experimental plan) will be discussed in this framework**.

The following individual topics are already identified:

- Interactions of **single organic molecules with cementitious phases**
- Interactions of **mixtures of organic molecules with cementitious phases**
- Interactions with the former systems, but **including metallic iron and/or its corrosion products**
- **Up-scaling to realistic materials** (cement pastes, concrete, reinforced systems) **and scenarios** (degradation of cement).

Main type of proposed studies by the organisations interested in this topic (Org-Cem(-Fe) system): Solubility, sorption and diffusion



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Bottom-up approach and modelling

- Each step is expected to be studied from **experiments to models** (conceptual, numerical).
- Interpretation of the experimental results: **definition and implementation of relevant mathematical models**. Possibility to readjust some experimental conditions
- This includes **aqueous speciation** altogether, **surface interactions** and **transfer properties**.

Some expected outcomes:

- ✓ Organics sorption models versus cement degradation
- ✓ Modelling of competitive effects between organics for sorption sites
- ✓ Reactive transfer models applied to hardened cement materials
- ✓ Organics-Iron interactions in cement porewater solutions: speciation model
- ✓ Organics-Iron interactions in cement systems: up-take models with respect to iron corrosion products and cement phases

Direct input/link to CORI WP4 *"Modelling, upscaling, application to PA"*

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EXAMPLES

ROCKLAB

(1) a unique experimental system (ROCKLAB) emphasizes the need to carry out experiments under conditions similar to the real environment also in lab scale (respecting anoxic mode)

(2) non-invasive (intact) sampling in order to keep the running experiment being unchanged during sampling as well as the possibility of wireless and on-line process monitoring for better and more complex performance assessment under lab condition in anoxic atmosphere.

(3) very important for objectivity and reliability of experiments for providing a complex view on interactions between organics, cementitious environment, iron, and radionuclides in complexes respectively.

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Thanks for your attention

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Scope of work

Cementitious environment

Bottom-up approach: From cement phases to actual cementitious systems.

Cement phases

- **C-S-H and CASH**: Calcium silicate hydrate phases with different C/S ratios (Al, as org-Al interactions seem to be important)
- **Ettringite**: Ferrite-aluminate-tri-substituted
- **Monosulphate**: Ferrite-aluminate-monosubstituted

CEM formulation

- **CEM I** Ordinary Portland cement with a clinker composition ≥ 95%
- **CEM II** Portland cement with additions.
- **CEM III** Blended cement with BFS.
- **CEM IV** Pozzolanic cement
- **CEM V** Blended cement with BFS+FA+Pozzolanic additions.

Degraded CEM

1. **Fresh cement** (State I)
2. **Alkali-free cement**(State II, equilibrium with Portlandite)
3. **Portlandite-free cement** (State III, equilibrium with CSH)
4. **Degraded/Carbonated cement**

Structural systems

- **Systems including aggregates** (Mortars, Concrete)
- **Armoured systems:** Steel reinforcement in cementitiuos structures

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